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CONTACT CHARGE-TRANSFER EXCIMER LASERS

by

Ⓒ Amynmohammed Nurdin Dharamsi

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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ABSTRACT

Molecular charge-transfer complexes are examined with emphasis on their electronic states, potential energy curves and spectra. Potential energy curves are calculated for singlet and triplet states of several contact charge-transfer complexes, using the quantum chemistry method of Complete Neglect of Differential Overlap in Spectroscopy, CNDO/S. The Stoke's shifts that may be expected in these complexes are also calculated. Good agreement between the computed and experimentally available data is achieved.

It is shown that molecular contact charge-transfer complexes form a class of lasers analogous to the well-known rare-gas halide excimers. Although such complexes have been known for years to chemists, mainly from their work on absorption spectra, their potential as laser systems has not been previously investigated. The population inversion mechanism in contact charge-transfer lasers relies on picosecond radiationless relaxation of the lower state. This is a consequence of the additional degrees of freedom inherent in these relatively large polyatomic systems. The excimer systems which have been investigated to present, on the other hand, are mostly diatomics and having only one nuclear degree of freedom, rely on the repulsive nature or thermal dissociation of the ground electronic state for sustaining a population inversion.

Contact CT lasers would have radiative emission cross-sections and lifetimes of 10^{-17} cm^2 and 1μs in the visible or near u.v. and could, therefore, find use as storage lasers, for instance in laser driven nuclear fusion research. A pratical method for pumping such a laser is examined for one typical example and it is estimated that gains of several percent per cm may be expected.

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CHAPTER I

INTRODUCTION

Excimer lasers have recently generated a great amount of interest [1-4]. The bound-free electronic transitions inherent in excimers result in a tunable source of coherent radiation in the visible and near u.v. region of the electromagnetic spectrum. Such lasers have wide-ranging applications in several important areas of research including photophysics, photochemistry, isotope separation and soft coherent x-ray production by second and third order harmonic generation, to name a few. Further, several excimers which satisfy the basic requirements on fusion lasers [5-7], such as pulse duration (subnanosecond), wavelength (≈3000Å) and offer promise for future operation at the high peak powers ($\approx 10^{13}$W) necessary are being experimented upon.

The excimer lasers known today are mostly diatomics such as the rare-gas molecules Kr_2, Ar_2 Xe_2[9], the rare-gas halides [1,2], Hg_2 [8], and Na_2 [10]. The potential of other diatomic excimer lasers such as Na-Xe and Na-He is being investigated by some researchers [11]. Although many examples of the absorption spectra of polyatomic excimers and exciplexes are known [12,13,14], lasing has only been demonstrated in a few such complexes, by Mataga's group [15].

As mentioned above amongst the uses to which excimer lasers may be put is the possible application of some of them to nuclear fusion. At present, much effort is being directed in trying to achieve this by focussing a high energy short laser pulse on a microscopically small pellet containing hydrogen isotopes. A short Nd YAG laser pulse of about 1μm wavelength is amplified through an array of storage amplifiers and then focused on to the pellet. Recent results however indicate that a much shorter wavelength might prove more effective.

The rare gas halide laser is the only existing short wavelength laser with power and efficiency approaching that required for fusion experiments. However, this laser does not lend itself to generating short pulses. For example, a Nd YAG amplifier will store energy for several milliseconds and this stored energy is removed by passing a short pulse through the amplifier. Unfortunately, the rare-gas halide laser media will store energy for less than 10ns because the transitions, which operate between bound to repulsive states, are strongly allowed. A KrF* storage amplifier hence cannot be made.

In the present work we explore large molecule excimers, the contact charge transfer (CT) complexes, as they are known to photochemists. Such complexes have spin-allowed transitions with typical cross-sections and lifetimes of 10^{-17}cm^2 and 1μs, making them more suitable as storage lasers than the diatomic excimers. This work is based upon the semi-emperical quantum chemistry method known as the Complete Neglect of Differential Overlap in Spectroscopy (CNDO/S). The potential energy curves for several CT complexes between the oxygen molecule (acceptor) and small aromatic donor molecules are calculated. Very good agreement is obtained wherever experimental results exist. The possibility of emission in these CT complexes is examined, the Stoke's shifts that may be expected are calculated and emission wavelengths predicted.

It is shown that a population inversion in contact CT complexes can, in principle, be obtained once the excited CT state is accessed. The inversion mechanism relies on fast radiationless depopulation of the lower state which is possible in these relatively large and massive molecular systems. The additional degrees of freedom (as compared to the lone nuclear degree of freedom in a diatomic), available in such polyatomic excimers eliminates

The reliance on the repulsive nature, or the thermal dissociation, of the ground electronic state. A method of pumping such a laser is studied and applied to the pyrrole - O_2 system for which a gain of approximately $3x10^{-2}cm^{-1}$ is predicted.

1.1 Scope of this Work

Chapter II deals with charge-transfer theory including the theoretical and experimental aspects of contact CT complexes. This chapter is based mainly on R.S. Mulliken's pioneering work [16].

Chapter III outlines the general Linear Combination of Atomic Orbital-Molecular Orbitals (LCAO-MO) methods [17], including the Zero Differential Overlap (ZDO) approximation [18], of which the Complete Neglect of Differential Overlap (CNDO) Approximation [19] is a special case. Various formulations of the latter method, that is CNDO/1, CNDO/2 and CNDO/S [20-34] are outlined.

Chapter IV describes the application of CNDO/S to the complexes of benzene, aniline, pyrrole and H_2O with O_2. The computer program [34] used in these calculations is outlined. The results obtained are compared with experimental data available in the literature [36,37].

Chapter V examines the possibility of lasing action in contact CT amplifiers [38]. A method of pumping is studied, excited state quenching is examined and an estimate for the expected gain in a"typical"contact CT system made.

Chapter VI outlines future work that should be undertaken before a contact CT laser can be operated in the laboratory.

CHAPTER II

CHARGE-TRANSFER MOLECULAR COMPLEXES

2.1 Molecular Interactions and Bonding

It has been known for several years now that even valence saturated atoms and molecules interact with one another. Such interactions are generally of strength intermediate between the weak (generally less than 1Kcal/mole or 4×10^{-2}eV/molecule) long range forces of dispersion, including van der Waals interaction, and the strong (greater than 50Kcal/mole or 2eV/molecule) chemical bonding forces in stable molecules where classical valence saturation is sought [39].

This intermediate type of attractive force is responsible for the formation of molecular complexes whose existence was discovered when absorption spectra, not exhibited by either component alone, were found when two different molecules interacted [40,41].

Molecular complexes of this type themselves vary in bonding energies. Absorption spectra have been measured for very stable complexes as well as for complexes which have practically no binding energy in the ground state. In the latter case the components are merely "in contact" in Mulliken's terminology.

In the present work it is these contact charge-transfer (CT) complexes that will be focused upon. Mulliken has shown that the intensity of contact CT complexes can be relatively large and since no stable ground state exists the possibility of excimer radiation immediately becomes obvious. This aspect is treated in Chapter V.

Mulliken's CT theory which has been very successful in explaining the behaviour of these complexes will be outlined below, first in general terms and then for contact CT complexes.

All chemical bonds, however classified, (covalent, ionic, charge-transfer etc.) have several common features [52]. Thus, all bonds are formed because the potential energy of the molecular system is lowered as a result of electrons moving simultaneously near the positive charges of two or more nuclei. Electrons of one atom can move simultaneously near the positively charged nucleus of a second atom by entering a valence orbital of the latter which is either half-filled or vacant. Even when an atom has formed one or more bonds, it retains reactivity as long as there are additional half-filled or vacant valence orbitals. A chemical bond formed between two atoms each with a single half-filled valence orbital has a binding energy between 50-150Kcal/mole. A bond formed between an atom with a vacant valence orbital and an atom with an unused pair, will usually be in the range of 10-50Kcal/mole.Hence,although the classification of chemical bond types is very fruitful, the common underlying features nevertheless make such divisions somewhat artificial. With this in mind one may make the following definitions [52].

A covalent bond is formed when a pair of electrons is equally shared between two atoms. Some examples are the bonds in homonuclear diatomics such as O_2, N_2, H_2 etc.

A bond in which the shared electrons are concentrated nearer to one of the atoms is said to have ionic character. Some examples are the heteronuclear diatomics such as HCl, HF, NaCl etc.

Covalent bonds both with and without ionic character are bonds resulting from the proximity of two atoms which possess half filled valence orbitals [52].

The definition of charge-transfer bonding has been the subject of some controversy [53,59,60]. Although all molecules interact with other molecules, when, as in most cases, the intermolecular forces involved are small compared to the interatomic forces within molecules there is no difficulty in defining the molecule and concluding that inter-molecular forces are physical ("non chemical") in that they do not require a description in terms of classical covalent or ionic bonding. However, numerous examples are known where such interactions cannot be explained purely by invoking dipole-dipole,dipole-induced-dipole, higher order pole, or dispersion forces. The indisputable usefulness of the concept of the molecule has led to a reluctance in recognizing the possibility of graded interaction between the extremes of the classical covalent or ionic bond and the weaker lang range van der Waals interactions.

In this work a complex will be defined as a system formed by the interaction of two or more component molecules and/or ions. The complex may or may not be capable of existence in an independent form. Many complexes are, for instance, known to exist only in solution.

Some workers [52], prefer to distinguish charge-transfer (also called electron donor-acceptor) bonding from covalent and ionic bonding by restricting CT bonding to mean interactions which utilize completely vacant acceptor orbitals. This distinction can be somewhat misleading as illustrated by the fact that 0_2 forms CT bonds with numerous molecules with one of its half-filled antibonding molecular orbitals acting as an acceptor orbital.

The main criticism against the use of the term "charge-transfer" is that in many so-called charge-transfer complexes, charge transfer forces do not provide the major contribution to the binding forces in the ground state [59,60]. Mulliken, the founder of present day CT theory, pointed this out himself [16]. Nonetheless, the term has wide common usage in describing the molecular interactions to be treated here [53] and will hence be retained.

As pointed out below in the cases where the ground state is not charge transfer stabilized (contact CT complexes), the excited state generally is.

In the present work, a charge-transfer bond will be defined as a bond between two molecules (stable on their own) formed by the donation (to various degrees) of an electron from the least bound valence orbital of the donor molecule to the first (completely or partially) vacant valence orbital of the acceptor molecule [42,53]. The bond strength of such complexes in the ground electron state ranges from approximately 50Kcal/mole (for the very strong complexes) to practically zero for the contact CT complexes. We note here that contact CT complexes are important because they have stabilized excited states and radiative transition oscillator strengths which are relatively large compared to other CT complexes.

Charge transfer resonance forces [42] are (quite universal molecular) forces of attraction and they occur between like as well as unlike molecules. In this respect charge transfer forces resemble the dispersion forces that F. London used to successfully explain van der Waals attractions. CT forces supplement these dispersive and other attraction forces such as those due to dipole-dipole and dipole-induced dipole effects and help in explaining cohesion between molecules. They differ from these other attractive forces in that they fall off faster (exponentially, like valence forces) with increasing distance and they operate only if there is an appreciable overlap of the wave functions of the interacting molecules.

A very interesting feature of CT forces is that their orientational properties, which are a result of quantum mechanical symmetry requirements, often differ drastically from the orientational properties of other forces. Thus, CT forces have often been decisive in establishing modes of packing of molecules in crystals whose structures would otherwise not be intelligible.

2.2 Mulliken Charge-Transfer Theory [16,40-58]

The basis of the theory [44] is the idea that any two species, whether they are atoms, positive or negative ions, or molecules or even solids, have a tendency to exchange electrons, that is, to act as electron donors (denoted by D in this work) or electron acceptors (denoted by A). We note that either the donor or the acceptor or both may be, and very often are, closed shell (valence saturated) molecules [16].

For simplicity we consider here one to one associations. Furthermore the theory presented will be a vapor state theory. However, after small corrections for solvation energies, it remains essentially valid for solutions in inert solvents.

Quantum mechanically, the total ground state wavefunction of the combined donor-acceptor system may be approximated by:

$$\Psi_N(D\cdot A) \approx a\,\Psi_0(D,A) + b\,\Psi_1(D^+A^-) \tag{2.1}$$

The first term on the right hand side incorporates the "ordinary" interaction between atoms and molecules, such as London dispersion forces (including van der Waals forces) [42], and any electrostatic interactions between permanent or temporary dipole moments [44], that might be present. This term is hence called the no bond term. The second term expresses the condition where an electron has gone over from the donor to the acceptor, and is called the dative term. The dative structure corresponds to an ionic plus a covalent bond and has sometimes been called a semipolar double bond also [16]. Equation (2.1) could be made more accurate by including such terms as $c\,\Psi_2(D^-A^+)$ and locally excited terms such as $d\,\Psi_3(D^*,A)$, $e\,\Psi_4(D,A^*)$ etc. For the most part, however, the approximation given by (2.1) is adequate. The value of b^2 represents the amount of charge-transfer.

In loose complexes b^2 is much less than a^2. For instance in the benzene-I_2 complex $b^2 \approx 0.06$ and $a^2 \approx 0.94$.

If the ground state structure of a complex is expressed by Ψ_N, then quantum-mechanical principles dictate that there be an excited state Ψ_v given by [16]:

$$\Psi_v = -b^*\Psi_0(D,A) + a^*\Psi_1(D^+A^-) \tag{2.2}$$

This excited state is the charge transfer (CT) state.

In loose complexes, by definition, the ground state is mostly no-bond $(|a|^2 >> |b|^2$ and the excited state is therefore mostly dative $(|a^*|^2 >> |b^*|^2)$. Hence, in these cases the excited CT state essentially corresponds to the condition where an electron has been transferred from the donor D to the acceptor A.

The normalizing conditions:

$$\int \Psi_N(D\cdot A)\ \Psi_N(D\cdot A)dv = 1 \tag{2.3}$$

and

$$\int \Psi_v(D\cdot A)\ \Psi_v(D\cdot A)dv = 1 \tag{2.4}$$

where the integrations are over all coordinate space yield:

$$a^2 + b^2 + 2abS_{01} = 1 \tag{2.5}$$

and

$$(a^*)^2 + (b^*)^2 - 2a^*b^*S_{01} = 1 \tag{2.6}$$

S_{01} is the non-orthogonality or overlap integral of the wavefunctions Ψ_0 and Ψ_1

$$S_{01} = \int \Psi_0\Psi_1 dv \tag{2.7}$$

Note that we have used the normalizing conditions [16]

$$\int \Psi_0(D,A)\ \Psi_0(D,A)dv = 1 \qquad (2.8)$$

and

$$\int \Psi_1(D^+A^-)\Psi_1(D^+A^-)dv = 1 \qquad (2.9)$$

in deriving equations (2.5) and (2.6).

An important requirement is that Ψ_0 and Ψ_1 belong to the same group theoretical symmetry species, in terms of the symmetry of the complex. In other words, Ψ_0 and Ψ_1 must belong to the same irreducible representation of the point group to which the complex belongs. This requirement is the consequence of the fact that the Hamiltonian operator must have the full symmetry of the complex since it is simply an operator expression for the energy of the system, and this energy cannot change in either sign or magnitude as a result of a symmetry operation. The Hamiltonian therefore belongs to the totally symmetric representation. Hence [61,62,63] expressions such as

$$H_{01} = \int \Psi_0^* \mathcal{H} \Psi_1 \, dv \qquad (2.10)$$

which determine the amount of resonance energy stabilization [41,44] would be zero if Ψ_0 and Ψ_1 belonged to different symmetry species of the complex.

If $\mathcal{H}$ is the total Hamiltonian of the complex then the time independent Schroedinger Equation for the system [17,64] is as

$$\mathcal{H}\Psi = E\Psi \qquad (2.11)$$

where Ψ and E are the energy eigenfunction and eigenvalue respectively.

Using the expression given by (2.1) for the eigenfunction in (2.11) we obtain

$$(\mathcal{H}-E)\ (a\Psi_0 + b\Psi_1) = 0 \qquad (2.12)$$

Premultiplying by the complex conjugate of Ψ_0, Ψ_0^*, and integrating over all coordinate space yields

$$a(H_{00}-E) + b(H_{01}-S_{01}E) = 0 \qquad (2.13)$$

where

$$H_{00} = \int \Psi_0^{*} \mathcal{H} \Psi_0 dv \equiv <\Psi_0|\mathcal{H}|\Psi_0> \overset{\Delta}{=} E_0 \qquad (2.14)$$

$$H_{01} = \int \Psi_0^{*} \mathcal{H} \Psi_1 dv \equiv <\Psi_0|\mathcal{H}|\Psi_1> \overset{\Delta}{=} E_{01} \qquad (2.15)$$

Similarly premultiplying (2.12) by Ψ_1^{*} and integrating over all space yields

$$a(H_{10}-S_{01}E) + b(H_{11}-E) = 0 \qquad (2.16)$$

where

$$H_{10} = \int \Psi_1^{*} \mathcal{H} \Psi_0 dv \equiv <\Psi_1|\mathcal{H}|\Psi_0> \overset{\Delta}{=} E_{10} \qquad (2.17)$$

and

$$H_{11} = \int \Psi_1^{*} \mathcal{H} \Psi_1 dv \equiv <\Psi_1|\mathcal{H}|\Psi_1> \overset{\Delta}{=} E_1 \qquad (2.18)$$

(Normally one would be dealing with real functions and consequently the complex conjugate symbol may be dropped).

It can be shown that

$$H_{01} = H_{10} \overset{\Delta}{=} E_{01} \qquad (2.19)$$

Now equations (2.15) and (2.16) have a non trivial solution if the following condition is satisfied.

$$\begin{matrix} E_0 - E & E_{01} - S_{01}E \\ E_{01} - S_{01}E & E_1 - E \end{matrix} = 0 \qquad (2.20)$$

Expanding this quadratic in E yields

$$E^2(1-S_{01}^2) + E(2S_{01}E_{01}-E_0-E_1) + E_0E_1-E_{01}^2 = 0$$

Solving for E and multiplying by $(1-S_{01}^2)$ yields

$$E(1-S_{01}^2) = \frac{E_0+E_1}{2} - S_{01}E_{01} \pm \frac{1}{2}[(2S_{01}E_{01}-E_0-E_1)^2 - 4(1-S_{01}^2)(E_0E_1-E_{01}^2)]^{1/2}$$

$$E(1-S_{01}^2) = (\tfrac{1}{2})\ (E_0+E_1) - S_{01}E_{01} \pm [(\Delta/2)^2 + \beta_0\beta_1]^{1/2} \qquad (2.21)$$

where

$$\Delta = E_1-E_0 \qquad (2.22)$$

$$\beta_0 = E_{01}-E_0S_{01} \qquad (2.23)$$

$$\beta_1 = E_{01}-E_1S_{01} \qquad (2.24)$$

and

$$\beta_1-\beta_0 = - S_{01}\Delta \qquad (2.25)$$

If the ground state energy (the "normal" state) is denoted by E_N and the excited state by E_V then from (2.21)

$$E_V-E_N = h\nu_{CT} = \frac{2[(\Delta/2)^2 + \beta_0\beta_1]^{1/2}}{1 - S_{01}^2} \qquad (2.26)$$

where

ν_{CT} denotes the frequency of the charge-transfer spectrum line.

From (2.13), by substituting E_N for E

$$\frac{b}{a} \triangleq \rho = - \frac{(E_0-E_N)}{H_{01}-S_{01}E_N} \qquad (2.27)$$

and from (2.16)

$$\frac{b}{a} \triangleq \rho = - \frac{(E_{10}-S_{01}E_N)}{(E_1-E_N)} \qquad (2.28)$$

Similarly

$$\frac{b^*}{a^*} \triangleq \rho^* = \frac{(E_{01}-S_{01}E_V)}{E_0 - E_V} = \frac{(E_1-E_V)}{E_{01}-S_{01}E_V} \qquad (2.29)$$

Equation (2.1) can be rewritten as

$$\frac{\Psi_N}{a} = \Psi_0 + \rho\ \Psi_1$$

and from the normalization condition (2.5) we obtain

$$1 + \rho^2 + 2\rho\ S_{01} = \frac{1}{a^2}$$

therefore

$$\Psi_N = \frac{\Psi_0 + \rho\Psi_1}{[1 + \rho^2 + 2\rho S_{01}]^{1/2}} \tag{2.30}$$

Similarly

$$\Psi_V = \frac{\Psi_1 - \rho^*\Psi_0}{[1 + \rho^{*2} - 2\rho^* S_{01}]^{1/2}} \tag{2.31}$$

2.2.1 Loose CT Complexes

For weak complexes $S_{01}^2 << 1$ as mentioned previously. (Mulliken [16] defines these complexes as those for which $S_{01} \lesssim 0.1$). Then we can write from equation (2.20),

$$\begin{vmatrix} E_0 - E_N & E_{01} \\ E_{01} & E_1 - E_N \end{vmatrix} \approx 0$$

Hence

$$E_N \approx E_0 - \frac{E_{01}^2}{E_1 - E_N}$$

$$= E_0 - \frac{E_{01}^2}{(E_1 - E_0) + (E_0 - E_N)}$$

Further for such weak complexes we can write, from (2.23),

$$\beta_0 \approx E_{01}$$

Therefore, using equation (2.22)

$$E_N \approx E_0 - \frac{\beta_0^2}{\Delta} \tag{2.32}$$

where we have also used the fact that for weak complexes the resonance energy in the ground state due to the no bond and normal wavefunctions Ψ_0

and Ψ_N, given by E_0-E_N, is small [41]. Similar arguments lead to

$$E_V = E_1 + \frac{\beta_1^2}{\Delta} \qquad (2.33)$$

The CT absorption frequency would hence be

$$h\nu_{CT} = E_V-E_N = \Delta + \frac{\beta_0^2 + \beta_1^2}{\Delta} \qquad (2.34)$$

This expression is valid for loose complexes and may be compared to the somewhat more involved general expression (2.26) derived above which is valid for both strongly and loosely bound complexes.

The charge transfer resonance energy stabilization of the ground state is, from equation (2.32), $-\beta_0^2/\Delta$. The CT resonance energy for the upper state is, from (2.33), $+\beta_1^2/\Delta$.

From equation (2.28)

$$\frac{b}{a} = \rho = -\frac{E_{10}}{E_1-E_0+E_0-E_N} = -\frac{E_{10}}{\Delta} = -\frac{\beta_0}{\Delta} \qquad (2.35)$$

and similarly from equation (2.29)

$$\frac{b^*}{a^*} = \rho^* = -\frac{\beta_1}{\Delta} \qquad (2.36)$$

The wavefunctions of the ground and excited CT states are then obtained by substituting these expressions for ρ and ρ^* into equations (2.30) and (2.31) above.

2.2.2 Emperical Formulation of Loose CT Complexes Theory

In order to test the above theory Mulliken derived an expression for the CT absorption frequency in terms of emperical quantities such as ionization potentials and electronic affinities.

Figure 2.1 [16] shows the general shape of the potential energy curves of a CT complex whose wavefunctions are given by equations (2.1) and (2.2).

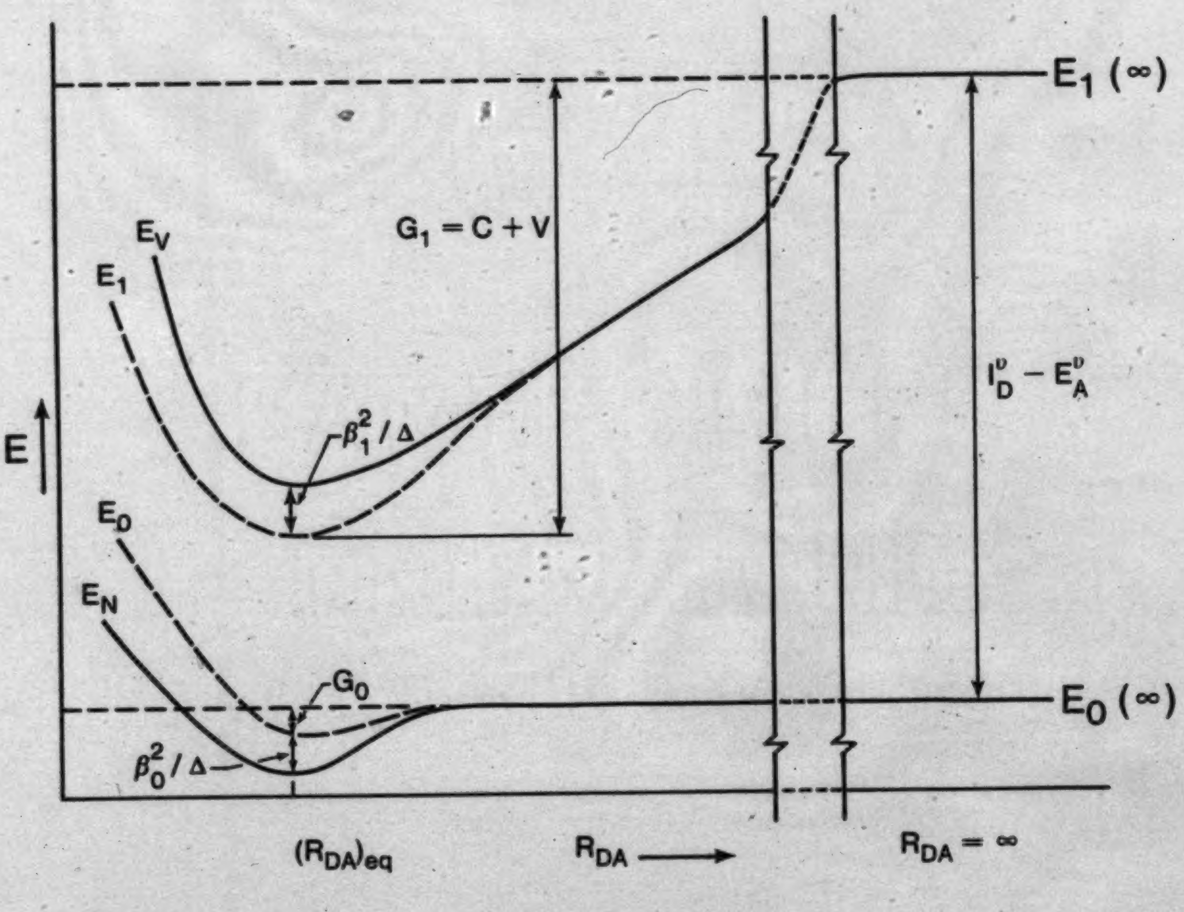

$E_1(\infty)$
$G_1 = C + V$
E_V
E_1
$I_D^v - E_A^v$
E
β_1^2/Δ
E_D
E_N
G_0
$E_0(\infty)$
β_0^2/Δ
$(R_{DA})_{eq}$
R_{DA} →
$R_{DA} = \infty$

Fig.2.1 The energies E_v and E_N as functions of the donor-acceptor separation R_{DA} [16].

R_{DA} is the distance between the donor and acceptor molecules. When $R_{DA}=\infty$ (i.e. the donor and acceptor are not interacting) the energy difference E_1-E_0 (see equations (2.21) and (2.22)) is simply the difference between the ionization energy of the donor, D, and the electron affinity of the acceptor molecule A.

$$E_1 - E_0 \Big|_{R_{DA}\to\infty} = I_D^V - E_A^V \tag{2.37}$$

The superscript V stands for "vertical". I_D^V is the ionization potential for the free donor molecule constrained to remain, after ionization, in the conformation it has in its neutral ground state (that is the internal coordinates of the ionic state are the same as those of the neutral normal state). E_A^V is the electron affinity of the similarly constrained acceptor.

The quantity G_1 applies to the dative structure denoted by Ψ_1 and has two components.

$$G_1 = C + V \tag{2.38}$$

where

C is the Coulomb energy that is dissipated when the D^+ and A^- ions are brought together at the equilibrium separation. C also includes two smaller terms, generally neglected, due to polarization and exchange repulsion.

V is the energy of formation of the valence bond in the dative state.

G_0 represents the interaction of D and A if they were brought together in the no-bond structure Ψ_0. This includes the London dispersion forces and any interactions between permanent or temporary dipole moments that may be present. In treating loose complexes G_0 is small and generally may be ignored [16]. $-\beta_0^2/\Delta$ and $+\beta_1^2/\Delta$ are the CT resonance energy terms described above. Hence β_0, β_1 are also called resonance integrals.

From Figure 2.1 we write

$$\Delta = E_1 - E_0 = I_D^V - E_A^V + G_1 - G_0 \qquad (2.39)$$

We define

$$X_1 = E_V - E_1 \qquad (2.40)$$

$$X_0 = E_N - E_0 \qquad (2.41)$$

The energy of formation of the complex in the ground state is, therefore,

$$\Delta E_f = G_0 + X_0 \qquad (2.42)$$

$$h\nu_{CT} = E_V - E_N = E_1 - E_0 + E_V - E_1 + E_0 - E_N$$

Hence using (2.39), (2.4) and (2.41)

$$h\nu_{CT} = I_D^V - E_A^V + G_1 - G_0 + X_1 - X_0 \qquad (2.43)$$

Equation (2.43) is general and applies to both strong and weak CT complexes. In the former case (2.43) should be used in equation (2.26) while in the latter case it may be used in (2.34).

For a series of weak complexes between a set of donor molecules and a single acceptor, E_A^V is constant. It has been standard practice to assume that G_1 is approximately constant although it has been shown [16] that the Coulombic component of , C, this quantity may vary appreciably with the size of D, for aromatic donors at least. Also, for similar donors G_0 is taken to be constant (usually neglected since it is small in weak complexes). Finally, for weak complexes of a single acceptor with similar donors it is [16] also assumed that the integral β_0 and the overlap integral S_{01} are relatively constant and small in magnitude. Hence, for a set of closely related weak complexes of a single acceptor we can write from equation (2.34)

$$h\nu_{CT} \simeq \Delta + \frac{C_2}{\Delta} \tag{2.44}$$

where

$$C_2 = \beta_0^2 + \beta_1^2 \tag{2.45}$$

Further defining the parameter C_1 as

$$C_1 = I_D - \Delta \tag{2.46}$$

and using equation (2.39)

$$C_1 = I_D - \Delta = (I_D - I_D^V) + E_A^V - G_1 + G_0 \tag{2.47}$$

Using (2.46) in (2.44) we obtain

$$h\nu_{CT} \simeq \Delta + \frac{C_2}{\Delta} = I_D - C_1 + \frac{C_2}{I_D - C_1} \tag{2.48}$$

We note that (2.47) involves explicitly the difference between the vertical ionization potential I_D^V and the adiabatic ionization potential I_D. The latter is the energy difference between the donor ion in its ionic equilibrium configuration and the donor molecule in its neutral molecular configuration. This is in contrast to the vertical ionization potential, defined above, in which the donor ion is constrained to remain in the configuration it has in its neutral normal (ground) state. For most molecules (e.g. benzene) the equilibrium geometry of the ion is not expected to be very different from that of the neutral molecule. Therefore, it is normally assumed that

$$I_D - I_D^V \simeq 0 \tag{2.49}$$

However, in other cases where it is known that the ionic configuration is substantially different from that of the molecule, (2.49) cannot be used. For example for the amines the ionic equilibrium configuration is believed to be planar rather than pyramidal as for the molecule. In this case, it has been estimated [16] that the difference between the vertical and adiabatic ionization potentials could be as high as half an electron volt.

Experimental measurements of the absorption spectra [65,66] for sets of chemically related donors with various acceptors have, in general, been in good agreement with equation (2.48). Estimates for the constants C_1 and C_2 for several groups of CT complexes have been made from such measurements.

2.3 Intensities of Charge Transfer Spectra

The theoretical treatment of the intensities of CT complexes including contact CT complexes (see section 2.4 below) requires the formulation of the wavefunctions of the no-bond and dative structures (Ψ_0 and Ψ_1) and the evaluation of their overlap integral S_{01}. [16,67].

2.3.1 Detailed forms of no-bond and dative wavefunctions

The no bond wave function $\Psi_0(D,A)$, defined in equation (2.1), may be written as follows

$$\Psi_0^{[N]}(D,A) = (\Psi_{mod}^{[1..M]}(D)) \cdot (\Psi_{mod}^{[M+1..N]}(A)) \qquad (2.50)$$

Here the complex has a total of N electrons, the donor,D, has M electrons and the acceptor, A, N-M electrons, as indicated by the superscripts. The subscript "mod" stands for "modified". Hence, $\Psi_{mod}(D)$ is the wavefunction of the normal state of the donor molecule as it would be if the configuration of the free donor were modified to the nuclear framework which it has in the complex. $\Psi_{mod}(D)$ also incorporates the effects of exchange repulsion, dispersion and classical electrostatic attraction forces due to the presence of the acceptor A. $\Psi_{mod}(A)$ has a corresponding meaning. It is also understood that both $\Psi_{mod}(A)$ and $\Psi_{mod}(D)$ are antisymmetric with respect to the exchange of any two of their electrons. The overall wavefunction $\Psi_0(D,A)$

is antisymmetric in all the N electrons of the complex. The modification necessary to the free donor and acceptor wavefunctions depends on the strength of the interaction (or the CT bond in the normal state) being greater the stronger the bond.

Both $\Psi_{mod}(A)$ and $\Psi_{mod}(D)$ are approximated by a single Antisymmetrized Molecular Spin Orbital Product (AS.MSOP) function as follows

$$\Psi_0=\Psi_{mod}(D)\Psi_{mod}(A)=[\Psi_d(1)\alpha(1)\Psi_d(2)\beta(2)\Psi'_d(3)\alpha(3)\ldots\Psi_a(M+1)\alpha)M+1)\Psi_a(M+2)\beta(M+2)\Psi'_a(M+3)\alpha(M+3)\ldots] \tag{2.51}$$

Here Ψ_d refers to one of the molecular orbitals (MO's) on the donor, Ψ'_d to another and so on. Ψ_a and Ψ'_a refer to MO's on the acceptor. As mentioned above these are modified in comparison with MO's of the free donors and acceptors, but only slightly, in weak complexes, to which we address ourselves.

The dative wavefunction $\Psi_1(D^+A^-)$ can be expressed [67] in terms of two wavefunctions Ψ_I and Ψ_{II}

$$\Psi_1(D^+A^-) = \frac{\Psi_I + \Psi_{II}}{[2(1+S_I S_{II})]^{1/2}} \tag{2.52}$$

Ψ_I differs from Ψ_0 only in that an electron (for instance electron number 2) has been removed from the spin orbital $\Psi_a\beta$ of the donor and placed in the spin orbital $\Psi_a-\beta$ of the acceptor. The acceptor MO which accepts the electron is called Ψ_a- because in the wavefunction Ψ_1 it is an MO of the negative ion A^- (in the usual case where D and A are neutral molecules). Hence, Ψ_I is represented as follows

$$\Psi_I=\Psi^{(\alpha)}_{mod}(D^+)\Psi^{(\beta)}_{mod}(A^-)=[\Psi_d(1)\alpha(1)\Psi_{a-}(2)\beta(2)\Psi'_d(3)\alpha(3)\ldots \Psi_a(M+1)\alpha(M+1)\Psi_a(M+2)\beta(M+2)\Psi'_a(M+3)\alpha(M+3)\ldots] \tag{2.53}$$

Ψ_{II} differs from Ψ_I only in that electron 1 with α spin from Ψ_d, instead of electron 2 with β spin, occupies the vacant acceptor orbital Ψ_{a^-}. Hence,

$$\Psi_{II}=\Psi_{mod}^{(\beta)}(D^+)\Psi_{mod}^{(\alpha)}(A^-)=[\Psi_{a-}(1)\alpha(1)\Psi_d(2)\beta(2)\Psi_d'(3)\alpha(3)\ldots$$

$$\Psi_a(M+1)\alpha(M+1)\Psi_a(M+2)\beta(M+2)\Psi_a'(M+3)\alpha(M+3)\ldots] \quad (2.54)$$

In equation (2.52), $S_{I\ II}$ is the overlap integral function of the components Ψ_I and Ψ_{II} of the dative function Ψ_1. Hence,

$$S_{I\ II} = \int \Psi_I\Psi_{II}\ dv \equiv <\Psi_I|\Psi_{II}> \quad (2.55)$$

Substituting (2.53) and (2.54) into (2.55) yields

$$S_{I\ II}= \int[\Psi_d(1)\alpha(1)\Psi_{a-}(2)\beta(2)\Psi_d'(3)\alpha(3)\ldots$$

$$\Psi_a(M+1)\alpha(M+1)\Psi_d(M+2)\beta(M+2)\Psi_a'(M+3)\alpha(M+3)\ldots] \times$$

$$[\Psi_{a-}(1)\alpha(1)\Psi_d(2)\beta(2)\Psi_d'(3)\alpha(3)\ldots$$

$$\Psi_a(M+1)\alpha(M+1)\Psi_a(M+2)\beta(M+2)\Psi_a'(M+3)\alpha(M+3)\ldots]dv \quad (2.56)$$

Recognizing the orthonormalization condition for molecular spin orbitals, i.e. using

$$<\Psi_d(i)|\Psi_a(i)> = 1 \quad (2.57)$$

and

$$<\alpha(j)|\alpha(j)> = 1 \quad (2.58)$$

etc, equation (2.56) reduces to

$$S_{I\ II} = \int[\Psi_d(1)\Psi_{a-}(2)\Psi_{a-}(1)\Psi_d(2)dv' \quad (2.59)$$

where now the integration is over spatial coordinates, V', only.

Defining the overlap between the donor and acceptor orbitals as S_{da-}

$$S_{da-} = \int \Psi_d(i)\ \Psi_{a-}(i)\ dv' \tag{2.60}$$

equation (2.59) can be written as

$$S_{I\ II} = S_{da-}^2 \tag{2.61}$$

This follows because in (2.59) the integration is over six spatial coordinates, that in (2.60) is over three. Using (2.52) and (2.61) in (2.7), the overlap integral between the no bond and dative wavefunctions becomes

$$S_{01} = \int \frac{\Psi_0(\Psi_I + \Psi_{II})}{[2(1 + s_{da-}^2)]^{1/2}} \tag{2.62}$$

$$\int \Psi_0 \Psi_I dv = \int [\Psi_d(1)\alpha(1)\Psi_d(2)\beta(2)\Psi_d'(3)\alpha(3)\ldots$$

$$\Psi_a(M+1)\alpha(M+1)\Psi_a(M+2)\beta(M+2)\Psi_a'(M+3)\alpha(M+3)\ldots] \times$$

$$[\Psi_d(1)\alpha(1)\Psi_{a-}(2)\beta(2)\Psi_d'(3)\alpha(3)\ldots$$

$$\Psi_a(M+1)\alpha(M+1)\Psi_a(M+2)\beta(M+2)\Psi_a'(M+3)\alpha(M+3)\ldots] \tag{2.63}$$

Using (2.57) and (2.58) in (2.63) yields

$$\int \Psi_0 \Psi_I\ dv = \int \Psi_d(2)\ \Psi_{a-}(2)\ dv' = S_{da-} \tag{2.64}$$

Similarly

$$\int \Psi_0 \Psi_{II}\ dv = \int \Psi_d(1)\ \Psi_{a-}(1)\ dv' = S_{da-} \tag{2.65}$$

Using (2.64) and (2.65) in (2.62) yields

$$S_{01} = \sqrt{2}\,[1 + S_{da-}^2]^{-1/2}\, S_{da-} \qquad (2.66)$$

In the case of weak complexes the overlap integral S_{da-} is small enough to make the approximation

$$S_{01} \approx \sqrt{2}\, S_{da-} \qquad (2.67)$$

fairly accurate [56].

2.3.2 On the separation of electronic and nuclear motions

To treat the intensity of the CT spectrum of a complex expressions for the dipole and transition moments must be derived. We note here that the wavefunctions Ψ_0, Ψ_1, Ψ_N, Ψ_V, Ψ_I and Ψ_{II} describe the combined motion of the electrons and the nuclei. Further we note that when Ψ_0 and Ψ_1 are expressed as AS.MSOP functions such as (2.51)(2.53) and (2.54), Born-Oppenheimer separtion of nuclear and electronic motions [68-72] is implicitly assumed. The Born-Oppenheimer Approximation allows the total wavefunction of a molecular system to be separated into the product of nuclear and electronic wavefunctions. The total energy is also separable in this approximation, into the sum of nuclear and electronic energies. The nuclear motion of the system is generally then separated into vibrational and rotational motions. The validity of this approximation allows potential energy diagrams to be drawn for any molecular system [72].

The total wavefunction, Ψ_m^V, is expressed as a product of an electronic wavefunction, $\Psi_m(\bar{r}_i, \bar{R}_k)$, and a nuclear wavefunction $\Psi_q^m(R_k)$

$$\Psi_m^q = \Psi_m(\bar{r}_i, \bar{R}_k)\, \Psi_q^m(\bar{R}_k) \qquad (2.68)$$

where

q refers to an appropriate set of nuclear quantum numbers m denotes the electronic state of the molecular system, and the vectors $\bar{r}_i$ and $\bar{R}_k$ are the electronic and nuclear coordinates respectively.

As mentioned above the nuclear wavefunction, $\Psi^m_q(\bar{R}_k)$ is generally split into a product of vibrational and rotational wavefunctions. In loose complexes (which have a shallow potential energy minimum in the ground electronic state) consideration of the nuclear vibrational (and rotational) energies may become especially important since in these cases the vibrational quanta are small and the first few vibrational states would hence be populated under ordinary conditions (room temperature and pressure).

In contrast to molecular complexes (strong and weak) which exhibit minima in the ground electronic states, the nuclear kinetic energy of contact CT complexes (see section 2.4 below) which do not have a potential well cannot be classified into rotational and vibrational energies. (Of course each component of the complex may, and usually does, have vibrational and rotational motion of its own).

2.3.3 Transition and Dipole Moments

The transition moment for a spectroscopic transition between two rovibronic states m and n is given by

$$U^{q_m q_n}_{mn} = \langle \Psi^q_m | \bar{U}_{op} | \Psi^q_n \rangle \tag{2.69}$$

$$U^{q_m q_n}_{mn} \equiv \int \Psi^q_m \bar{U}_{op} \Psi^q_n d\bar{r}_i d\bar{R}_k \tag{2.70}$$

The term rovibronic [73] is here used to imply the total wavefunction (incorporating electronic, vibrational and rotational energies). $\bar{U}_{op}$ is the dipole moment operator and is given by

$$\overline{U}_{op} = e \sum_{k} z_k \overline{R}_k - e \sum_{i} r_i \tag{2.71}$$

where

z_k is the charge on the kth nucleus in the system, and the summations are over the total number of nuclei and electrons.

Using (2.68) in (2.69) yields

$$U_{mn}^{q_m q_n} = \int \Psi^{m}_{q_m} \left[\int \Psi_m \overline{U}_{op} \Psi_n d\overline{r}_i\right] \Psi^{n}_{q_n} d\overline{R}_k \tag{2.72}$$

Integration over the electronic coordinates defines the electronic transition moment $U^{el}_{mn}(\overline{R}_k)$ where

$$U^{el}_{mn}(\overline{R}_k) = \int \Psi_m(\overline{r}_i,\overline{R}_k)\overline{U}_{op}\Psi_n(\overline{r}_i,\overline{R}_k)d\overline{r}_i \tag{2.73}$$

The dipole moment of the normal (ground) state is obtained from (2.69) by substituting m=n=N and $q_m = q_n = q$. Carrying out the integration over electronic coordinates only first

$$\int \Psi_m \overline{U}_{op} \Psi_m d\overline{r}_i = \int \Psi_m (e \sum_{k} z_k \overline{R}_k - \sum_{i} e r_i) \Psi_m \, d\overline{r}_i$$

$$= e \sum_{k} z_k \overline{R}_k \int \Psi_m \Psi_m d\overline{r}_i - \sum_{i} e \int \Psi_m \overline{r}_i \Psi_m \, d\overline{r}_i$$

$$\int \Psi_m \overline{U}_{op} \Psi_m d\overline{r}_i = e \sum_{k} z_k \overline{R}_k - e\, N \langle \overline{r}^{q} \rangle \tag{2.74}$$

where

$\langle \overline{r}^{q} \rangle$ is the expectation value of the electronic positions

N is the total number of electrons, and we have used the normalizing condition $\langle \Psi_m | \Psi_m \rangle = 1$.

The dipole moment of the ground state, U_N^q, can now be obtained by carrying out the integration over nuclear coordinates in (2.72).

$$U_N^q = e \int \Psi_q^m \Big(\sum_k z_k \bar{R}_k - N\langle \bar{r}^q \rangle\Big) \Psi_q^N \, d\bar{R}_k$$

$$= e \sum_k \int \Psi_q^N \bar{R}_k \Psi_q^N \, d\bar{R}_k - Ne\langle \bar{r}^q \rangle \int \Psi_q^N \Psi_q^N \, d\bar{R}_k$$

Therefore

$$U_N^q = e \sum_k \langle \bar{R}_k \rangle - Ne \langle \bar{r}^q \rangle \tag{2.75}$$

where

$\langle \bar{R}_k \rangle$ is the expectation value for the k nuclear coordinates and the nuclear wavefunctions are normalized.

In the present work, the nuclear motion in the complex will be ignored. Hence, the electronic wavefunction, $\Psi_m(\bar{r}_i, \bar{R}_k)$, in (2.68) will be taken to describe the total wavefunction, Ψ_m^q. Provided the Born-Oppenheimer Approximation holds, this can be done with the provision that the nuclear kinetic energy could then, if necessary, be added onto the electronic energy. The wavefunctions Ψ_N, Ψ_V, Ψ_0, Ψ_1, Ψ_I and Ψ_{II} in equations (2.1), (2.2) and (2.52) are in this approximation taken to be the appropriate Born-Oppenheimer electronic wavefunctions. The electronic transition moment of the CT transition (V←N) is then

$$\bar{U}_{VN}^{el} = \langle \Psi_N | \bar{U}_{op} | \Psi_V \rangle \tag{2.76}$$

$$= \int (a\,\Psi_0 + b\,\Psi_1)\, \bar{U}_{op}\, (a^*\Psi_1 - b^*\Psi_0) dr_1$$

$$= aa^*\bar{U}_{01}^{el} + ba^*\bar{U}_1^{el} - ab^*\bar{U}_0^{el} - bb^*\bar{U}_{01}^{el} \tag{2.77}$$

where

$$\bar{U}_{01}^{el} = \langle \Psi_0 | \bar{U}_{op} | \Psi_1 \rangle \tag{2.78}$$

$$\overline{U}_1^{el} = \langle\Psi_1|\overline{U}_{op}|\Psi_1\rangle \tag{2.79}$$

$$\overline{U}_0^{el} = \langle\Psi_0|\overline{U}_{op}|\Psi_0\rangle \tag{2.80}$$

Now the dative and no bond wavefunctions are orthonormalized [56], and hence

$$\langle\Psi_N|\Psi_V\rangle = 0, \; \langle\Psi_N|\Psi_N\rangle = \langle\Psi_V|\Psi_V\rangle = 1 \tag{2.81}$$

Using equations (2.1) and (2.2) in equations (2.81) we obtain

$$\int(a\Psi_0 + b\Psi_1)(a^*\Psi_1 - b^*\Psi_0)dv = 0$$

$$aa^*S_{01} - ab^* + a^*b - bb^*S_{10} = 0$$

Now $S_{01} = \int \Psi_0\Psi_1 \, dv = \int \Psi_1\Psi_0 \, dv = S_{10}$

Hence $b^*a = a^*b + S_{01}(aa^* - bb^*)$ (2.82)

Substituting (2.82) into (2.77) yields

$$\overline{U}_{VN}^{el} = a^*b(\overline{U}_1^{el} - \overline{U}_0^{el}) + (aa^* - bb^*)\;(\overline{U}_{01}^{el} - S_{01}\,\overline{U}_0^{el}) \tag{2.83}$$

The intensity of the CT absorption (and emission) band is proportional to the square of the magnitude of this transition moment ($|U_{VN}^{el}|^2$).

2.4 Contact Charge Transfer Complexes

The expression for transition moment given by equation (2.83) explains the existence of contact CT spectra. These are new spectra which occur even when there is no experimental evidence for the formation of a complex in the ground state. In this case there is no resonance interaction, the ground state being a completely no-bond state, where only dispersion (including van der Waal's) and electrostatic (due to permanent and, or induced dipoles) attraction are exhibited. In this case the coefficient b in equation (2.1) is equal to zero.

Equation (2.83) now reduces to

$$\overline{U}^{el}_{VN} = aa^{*}(\overline{U}^{el}_{01} - S_{01}\,\overline{U}^{el}_{0}) \tag{2.84}$$

The normalizing conditions in (2.81) and (2.8) yield

$aa^{*} = 1$ and, therefore,

$$\overline{U}^{el}_{VN} = (\overline{U}^{el}_{01} - S_{01}\,\overline{U}^{el}_{0}) \tag{2.85}$$

The right hand side of this equation is generally non zero. This leads to the very important conclusion [67] that every pair of molecules, whether or not they form a stable complex in the ground electronic state must possess a charge-transfer excited electronic state and a CT spectrum. Whether or not absorption (or emission) spectra due to these states are readily observable depends, amongst other things, on their location with respect to other absorption bands of the two molecules, and on their intensity.

Molecules which do not interact specifically to form complexes are said by Orgel and Mulliken [48] to be *in contact* and their spectra are called *contact charge transfer spectra.* In such cases the distance between the donor and acceptor is approximately equal to the van der Waal distance.

In contact CT complexes there is practically no overlap of the donor orbital, Ψ_d, and the highest filled orbital of the acceptor, Ψ_a. Hence,

$$\int \Psi_d \Psi_a \, dv = 0 \tag{2.86}$$

However, in these cases there can be, and usually is, a large overlap between the donor orbital and the acceptor orbital, Ψ_{a-} into which the donor electron is transferred during the CT transition. Hence even when equation (2.86) holds and there is little or no CT stabilization of the ground state, generally

$$S_{da-} = \int \Psi_d \Psi_{a-} \, dv \neq 0 \tag{2.87}$$

S_{da-} may have an appreciable magnitude simply because the orbital Ψ_{a-} is larger and spatially more diffuse than the orbital Ψ_a. (Ψ_{a-} is generally an antibonding orbital whereas Ψ_a is usually bonding or non bonding). Now the right hand side of (2.85) may be interpreted [16] as dipole moment generated when a charge $-eS_{01}$ is transferred from the donor orbital to the centre of the region of overlap of Ψ_d and Ψ_{a-}.

Hence,

$$\overline{U}^{el}_{01} - S_{01}\overline{U}^{el}_{0} \approx - eS_{01}(\overline{r}_{da-} - \overline{r}_d) \tag{2.88}$$

Where $\overline{r}_{da-}$ is the average position of the overlap charge $\Psi_d\Psi_{a-}$ and r_d the average position of the donated electron in Ψ_d on D before transfer. Using (2.66)

$$\overline{U}^{el}_{01} - S_{01}\overline{U}^{el}_{0} \approx - e\sqrt{2}[1 + S^2_{da-}]^{-1/2} S_{da-} (\overline{r}_{da-} - \overline{r}_d) \tag{2.89}$$

Now although, as pointed out above, S_{da-} is generally greater than zero, it is certainly less than one and normally S^2_{da-} is much less than unity. Hence from (2.85) and (2.89)

$$\overline{U}^{el}_{VN} \approx - \sqrt{2}\, e\, S_{da-} (\overline{r}_{da-} - \overline{r}_d) \tag{2.90}$$

An important class of contact CT spectra are those exhibited by O_2 when interacting with various organic molecules. In this case since the acceptor orbital is one of the partially filled antibonding orbitals of O_2

the sizes of Ψ_a and Ψ_{a-} are not very different. The explanation given above for the existence of contact CT spectra is hence not applicable.

Murrell [58,74,75] has provided an alternative explanation for contact CT band intensities which is probably more relevant in this case. According to this, the contact CT band derives its strength by borrowing intensity from a strongly allowed transition of either the donor or the acceptor molecules. Mulliken [49] has successfully used this idea to explain the relatively large intensities, corresponding to decadic molar extinction coefficients close to 100, that are exhibited by the contact CT spectra of O_2. It is thought that the contact CT band borrows its intensity from the strongly allowed transition between the donor ground state and the donor singlet excited state. In cases where the transition, in the donor, to the first excited state is forbidden (as is the case in benzene) the CT state borrows spectroscopic combining power from a higher singlet excited state or states.

CHAPTER III

MOLECULAR ORBITAL THEORY

3.1 Introduction

The fundamental aspect of an excimer laser is the bound-free type of electronic transition between a stable upper level and an unbound ground state. In any investigation of the suitability of a molecular complex as an excimer laser system, therefore, it is important to study the electronic states. The restriction that the ground electronic state not be bound is obviously satisfied by a truly large number of molecules for example those which have a closed electronic shell, valence-saturated structure and which, being very stable on their own, do not exhibit attractive stabilization forces (besides the weak long-range van der Waal's type forces). It then becomes important to investigate whether or not suitably placed bound excited electronic states exist. This requires calculation of the potential energy curves for the excited states of the molecular systems.

Information is required about the location of the upper state minimum, the states of the component monomers to which it correlates and the location of other electronic states with respect to the excimer state. Coupled with an estimate of the oscillator strength of the excimer transition, this information enbales one to predict the wavelength and intensity of the laser transition. Potential energy curves yield information on the possibility of pumping the laser state by cross-over from locally excited states and also give information on gain-reducing quenching mechanisms. If the kinetic rates of such processes can be estimated a rate equation may be set up, the solution of which would give an estimate for the gain to be expected.

Numerous methods for computing molecular electronic states, varying a great deal in usefulness and sophistication, are available. These can be divided into two broad categories namely, *ab initio* methods and semiemperical methods. The former may be described as "first-principle methods" in which the analysis is based on the Schroedinger equation. The Born-Oppenheimer Approximation is used to set up the molecular electronic Schroedinger equation and approximate methods of solution are sought. Semiemperical methods on the other hand [76] seek to use all available experimental data to build a theory which is simpler to implement computationally.

The most severe criticism of semiemperical methods has been the objection of some researchers that these methods are "little more than clever and fortuitous parameter fittings without any real foundation in the original molecular Schroedinger equation". However, very often in rigorously theoretical methods, significant insight into the nature of the processes involved is prevented by intricate mathematical formalism. In semiemperical techniques it is generally easier to sketch a pictorial outline of the physical and chemical processes involved and to predict which experimental characteristics play a more important role than others. Obviously, both methods have their uses and as often happens, the development of one has fruitful consequences for the other.

Attempts at bridging the gap between *ab initio* and semiemperical methods have recently been made by Freed [76] who has provided a theoretical foundation for semiemperical methods in molecular electronic structure calculations.

Further categorization of the methods of treating molecular electronic systems, their spectra and bonding behaviour, into the valence bond and molecular orbital theories can be made. Valence bond theory is due mainly to Heitler, London, Slater and Pauling [77-80] whereas molecular orbital theory was developed initially by Hund and Mulliken [81-84]. Briefly, in the former method electron wavefunctions are written for pairs of bonded nuclei whereas in the latter completely delocalized (over the whole molecular nuclear framework) wavefunctions are set up. As might be expected then, molecular orbital (m o) theory generally has greater success in explaining the spectra and other properties of molecules and complexes which have delocalised π electronic systems.

The CNDO/S method, used in this work, is a semiemperical molecular orbital theory which has had demonstrated success in explaining the spectra of several molecules and molecular complexes [18-38].

In this chapter CNDO molecular orbital methods, and the theories and assumptions on which such methods are based, will be discussed. The Born-Oppenheimer formulation and its resultant simplification of the Schroedinger wave equation is described. The orbital approximation is used to derive expressions for the electronic energy in terms of the Exchange and Coulomb integrals. The Variational Principle is then used to derive the Hartree-Fork equations from which the Roothaan equations are obtained by using Linear Combinations of Atomic Orbitals-Molecular Orbitals (LCAO-MO's).

The Zero Differential Overlap (ZDO) Approximation or the Neglect of Differential Overlap (NDO) Approximation, as it is also known, is treated. Finally, the various Complete Neglect of Differential Overlap (CNDO) parameterizations which follow by the application of NDO to the Roothaan equations are described [19, 85-87].

3.2 Born-Oppenheimer Simplification of the Molecular Schroedinger Equation

As is usual in any molecular orbital theory first the Born-Oppenheimer Approximation is invoked to write the electronic Schroedinger wave equation for the molecular system.

$$H^{el}(\bar{r}_i, \bar{R}_k)\ \Psi^{el}(\bar{r}_i, \bar{R}_k) = E^{el}(\bar{R}_k)\ \Psi^{el}(\bar{r}_i, \bar{R}_k) \qquad (3.1)$$

where

$$H^{el}(\bar{r}_i, \bar{R}_k) = T_e(\bar{r}_i) + V_{ee}(\bar{r}_i) + V_{en}(\bar{r}_i, \bar{R}_k) \qquad (3.2)$$

and

$$T_e(\bar{r}_i) = -\frac{h}{2M_e} \sum_{i=1}^{N_e} \nabla_i^2 \qquad (3.3)$$

$$V_{ee}(\bar{r}_i) = \sum_{(ij)} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} \qquad (3.4)$$

$$V_{en}(\bar{r}_i, \bar{R}_k) = \sum_{(ik)} -\frac{Z_k e^2}{|\bar{r}_i - \bar{R}_k|} \qquad (3.5)$$

$H^{el}(\bar{r}_i, \bar{R}_k)$ is the electronic Hamiltonian Operater of the system with $\bar{r}_i$, $\bar{R}_k$ denoting the vector coordinates of the ith electron and the kth nucleus.

$T_e(\bar{r}_i)$ is the total kinetic energy operator for the electrons in the molecular system.

$V_{ee}(\bar{r}_i)$ represents the Coulomb potential term for electron-electron interactions.

$V_{en}(\bar{r}_i, \bar{R}_k)$ represents the Coulomb potential term for electron-nuclear interactions.

$\Psi^{el}(\bar{r}_i, \bar{R}_k)$ is the total electronic wavefunction corresponding to $\Psi_m(\bar{r}_i, \bar{R}_k)$ in equation (2.68), $E^{el}(\bar{R}_k)$ is the total electronic energy of the system.

M_e is the mass of an electron.

Z_k is the charge on the kth nucleus and h is the normalized Planck constant.

In this approximation the total wavefunction is

$$\Psi^{total}(\bar{r}_i, \bar{R}_k) = \Psi^{el}(\bar{r}_i, \bar{R}_k)\, \Psi^{nu}(\bar{R}_k) \qquad (3.6)$$

where

$\Psi^{nu}(\bar{R}_k)$ corresponds to the nuclear wavefunction $\Psi_q^m(\bar{R}_k)$ in equation (2.68).

$\Psi^{nu}(\bar{R}_k)$ is an eigenfunction of the nuclear Schroedinger wave equation which is written as

$$H^{nu}(\bar{R}_k)\Psi^{nu}(\bar{R}_k) = E^n \Psi^{nu}(R_k) \qquad (3.7)$$

$$H^{nu}(\bar{R}_k) = T_n(\bar{R}_k) + V_{nn}(\bar{R}_k) + E^{el}(R_k) \qquad (3.8)$$

$$T_n(\bar{R}_k) = -\frac{h^2}{2} \sum \frac{1}{M_k} \nabla_k^2 \qquad (3.9)$$

$$V_{nn}(\bar{R}_k) = \sum_{(kl\ )} - \frac{Z_k Z_l}{|\bar{R}_k - \bar{R}_l|} \qquad (3.10)$$

$T_n(\bar{R}_k)$ is the total kinetic energy operator for the nuclei in the molecular system. $V_{nn}(\bar{R}_k)$ is the Coulomb potential term for nuclear-nuclear interactions, and M_k is the mass of the kth nucleus.

In the Born-Oppenheimer Approximation the total energy E^{tot}, of the system can be approximated to the eigenvalue E^n of equation (3.7)

$$E^{tot} \approx E^n \qquad (3.11)$$

In a treatment of electronic wavefunctions such as CNDO and other methods, the aim is to solve equation (3.1) for the electronic wavefunction $\Psi^{el}(\bar{r}_i, \bar{R}_k)$ and electronic energy $E^{el}(\bar{R}_k)$ of the system. Nuclear motion is neglected, it being kept in mind that the Born-Oppenheimer Approximation allows the solution for the total (nuclear plus electronic) energy of the system to be approximated by superposing on to $E^{el}(\overline{R}_k)$, the terms for nuclear kinetic and Coulombic energies (by equations 3.7-3.10), should the need arise.

3.3 The Orbital Approximation

Having separated nuclear and electronic motions by means of the powerful Born-Oppenheimer Approximation, it is necessary to somehow differentiate the motions of the various electrons in the molecular system. This is done [89-94] by approximating an n electron wavefunction, $\Psi(1,2,...n)$ (corresponding to Ψ^{el} in 3.6) as a product of n one-electron functions $\psi_1(1)$, $\psi_2(2)$, ... $\psi_n(n)$.

$$\Psi(1,2, ... n) = \psi_1(1)\ \psi_2(2)\ ....\ \psi_n(n) \qquad (3.12)$$

Each $\psi_i(i)$ on the right hand side is a function of the coordinates of the ith electron alone and is called a molecular orbital. The product function is often called a Hartree product. The probability density function $|\Psi|^2$ computed from (3.12) is then the product of one-electron probability densities $|\psi_i(i)|^2$. From probability theory, this can only be so when the events associated with each of the probabilities $|\psi_i(i)|^2$ occur independently of one another. Hence, physically the orbital approximation is equivalent to the assumption that the various one-electron molecular orbitals are independent of one another, or in other words, correlation between the various electrons is neglected. The Born-Oppenheimer Approximation applied to the total molecular wavefunction (as shown in equation 3.6) similarly separates nuclear and electronic motions.

3.3.1 Molecular Spin Orbitals

The one electron orbitals in (3.12) specify only the spatial distribution of each electron and in that respect are incomplete. In addition to spatial motion, described by $\psi_i(i)$ and reflected in its orbital angular momentum, an electron also possesses an additional intrinsic angular momentum which is a manifestation of relativistic effects identified with electron spin.

The spin angular momentum is represented by the vector operator $\overline{S}$ which has the components $\overline{s}_x$, $\overline{s}_y$ and $\overline{s}_z$. The spin operators all commute [19] with the general Hamiltonian operator. This is a useful property since it implies that the eigenfunction of the spin operators will also be the eigenfunctions (with different eigenvalues, in general) of the Hamiltonian [64]. The components $\overline{s}_x$, $\overline{s}_y$ and $\overline{s}_z$ all commute with the spin-squared operator $\overline{S}^2$ but not with each other [17,19]. Spin functions may therefore be chosen which are simultaneously the eigenfunctions of $\overline{S}^2$ and one of the components of $\overline{S}$ usually arbitarily taken as $\overline{s}_z$.

The spin operators are best defined in terms of their operation on the spin function $\overline{\alpha}(\xi)$ and $\overline{\beta}(\xi)$ where ξ are the spin coordinates (which are entirely independent of the spatial coordinates x, y and z) of the electron [18]:

$$\overline{s}_x\overline{\alpha}(\xi) = \frac{1}{2}\,\overline{\beta}(\xi) \tag{3.13}$$

$$\overline{s}_x\overline{\beta}(\xi) = \frac{1}{2}\,\overline{\alpha}(\xi) \tag{3.14}$$

$$\overline{s}_y\overline{\alpha}(\xi) = \frac{1}{2}\,i\overline{\beta}(\xi) \tag{3.15}$$

$$\overline{s}_y\overline{\beta}(\xi) = -\frac{1}{2}\,i\overline{\alpha}(\xi) \tag{3.16}$$

$$\overline{s}_z\overline{\alpha}(\xi) = \frac{1}{2}\,\overline{\alpha}(\xi) \tag{3.17}$$

$$\overline{s}_z\overline{\beta}(\xi) = -\frac{1}{2}\,\overline{\beta}(\xi) \tag{3.18}$$

$\alpha(\xi)$ and $\beta(\xi)$ are in units of $\frac{h}{2\pi}$ where h is Planck's constant and has the units of angular momentum (energy x time).

The complete wavefunction of a single electron is a product of a spatial function (like $\psi_i(i)$ in equation 3.12) and a spinfunction, and is called a spin-orbital. A given spatial orbital $\psi_i(i)$ may be associated with either α or β spin and hence may give rise to a maximum of two spin-orbitals $\psi_i(i)\overline{\alpha}(\xi)$ and $\psi_i(i)\overline{\beta}(\xi)$. The general form of the orbital approximation then becomes

$$\Psi(1,2, \ldots n) = \psi_1(1)\alpha(1)\psi_2(2)\beta(2)\psi_3(3)\alpha(3) \ldots \psi_n(n)\beta(n) \tag{3.19}$$

where the numbers 1,2 .... n specify the appropriate spatial or spin coordinates of the respective electron. Equation (3.19) is normally contracted to

$$\Psi(1,2, \ldots n) = \psi_1(1)\overline{\psi}_2(2) \ldots \psi_{n-1}(n-1)\overline{\psi}(n) \tag{3.20}$$

where the barred orbitals $\overline{\psi}_i(i)$ are β spin orbitals and the unbarred ones are α spin orbitals associated with them.

3.3.2 Slater Determinantal Wavefunctions, the Antisymmetry Principle and the Pauli Exclusion Principle.

An important characteristic of an electronic wavefunction is its behaviour under permutation of the constituent electrons. Since electrons are indistinguishable particles no physical property of the system can be affected by interchange of the coordinates of any two electrons. This implies that the probability density function Ψ^2 must remain unchanged under such a permutation. Hence there are only two possibilities

$$\Psi(1,2, \ldots\ldots i,j, \ldots\ldots n) = \pm\ \Psi(1,2, \ldots\ldots j,i, \ldots\ldots n) \qquad (3.21)$$

It can be shown [19] (see below also) that only the antisymmetric wavefunction is compatible with the Pauli Exclusion Principle. Hence

$$\overline{P}_{ij}\Psi(1,2, \ldots\ldots n) = -\ \Psi(1,2, \ldots\ldots n) \qquad (3.22)$$

where $\overline{P}_{ij}$ is a permutation operator which interchanges all the coordinates (spatial and spin) of electrons i and j.

We see that wavefunctions such as (3.19) do not satisfy this requirement. For instance if

$$\Psi(1,2) = \psi_1(1)\alpha(1)\psi_2(2)\beta(2) \qquad (3.23)$$

then

$$\overline{P}_{12}\Psi(1,2) = \psi_1(2)\alpha(2)\psi_2(1)\beta(1) \qquad (3.24)$$

and therefore

$$\overline{P}_{12}\Psi(1,2) \neq -\ \psi(1,2) \qquad (3.25)$$

However, if we write

$$\psi(1,2) = \begin{matrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) \end{matrix} \qquad (3.26)$$

i.e.

$$\Psi(1,2) = \psi_1(1)\alpha(1)\psi_1(2)\beta(2) - \psi_1(1)\beta(1)\psi_1(2)\alpha(2) \qquad (3.27)$$

then

$$\overline{P}_{12}\Psi(1,2) = \psi_1(2)\alpha(2)\psi_1(1)\beta(1) - \psi_1(2)\beta(2)\psi_1(1)\alpha(1) \qquad (3.28)$$

i.e.

$$\overline{P}_{12}\Psi(1,2) = -\Psi(1,2) \qquad (3.29)$$

which then satisfies the Antisymmetry Principle given by (3.22). To completely specify an electronic wavefunction in the orbital approximation, therefore it only remains to define $\Psi(1,2)$ in (3.26) such that it is normalized. Hence a two electron wavefunction can be completely specified by the following Slater determinant

$$\Psi(1,2) = \Pi \begin{matrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) \end{matrix} \qquad (3.30)$$

where Π is a normalizing constant.

For a closed shell system of 2n electrons where each spatial orbital contains the maximum possible two paired spin electrons the Slater determinant, which is the simplest orbital wavefunction that satisfies the Antisymmetry Principle is written as

$$\Psi(1,2,\ldots.2n) = \Pi \begin{matrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \ldots\ldots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \ldots\ldots & \psi_n(2)\beta(2) \\ \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots & \ldots\ldots\ldots \\ \psi_1(2n-1)\alpha(2n-1) & \psi_1(2n-1)\beta(2n-1) & \psi_2(2n-1)\alpha(2n-1) & .. & \ldots\ldots\ldots \\ \psi_1(2n)\alpha(2n) & \psi_1(2n)\beta(2n) & \psi_2(2n)\alpha(2n) & \ldots\ldots & \psi_n(2n)\beta(2n) \end{matrix} \qquad (3.31)$$

This is usually abbreviated as follows

$$\Psi(1,2,\ldots.2n) = |\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ \ldots\ \psi_n(2n)\beta(2n)| \qquad (3.32)$$

by using the diagonal terms in (3.31). Using bars for β spin functions, this is abbreviated further

$$\Psi(1,2,\ldots 2n) = |\psi_1(1)\bar{\psi}_1(2) \;\ldots.\; \bar{\psi}_n(2n)| \qquad (3.33)$$

Often the notation is simplified even further by dropping the identifying electron numbers

$$\Psi(1,2,\ldots .2n) = |\psi_1\bar{\psi}_1 \;\ldots.\; \bar{\psi}_n| \qquad (3.34)$$

Equations (3.32), (3.33) and (3.34) all imply (3.31), the normalizing constant being understood.

Another way to write a determinant such as that in equations (3.31) to (3.34) is as follows [19]:

$$\Psi(1,2,\ldots .2n) = \Pi \sum_{\bar{P}} (-1)^P \, \bar{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots.\psi_n(2n)\beta(2n)\} \qquad (3.35)$$

where the normalizing factor Π is explicitly shown, $\bar{P}$ is a permutation of 1,2,....2n and $(-1)^P$ is +1 or -1 for even or odd permutations respectively. For example the operator $\bar{P}$ which yields the permutation 3421 of the electrons 1234 has the property

$$\bar{P}_{3421}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\psi_2(3)\alpha(3)\psi_2(4)\beta(4)\}=\{\psi_1(3)\alpha(3)\psi_1(4)\beta(4)\psi_2(2)\alpha(2)\psi_2(1)\beta(1)\} \qquad (3.36)$$

and the permutation 3421 is odd because for instance, it can be written as a product of three separate permutations of electrons 4 and 2 ($\bar{P}_{42}$), 3 and 1 ($\bar{P}_{31}$) and finally 1 and 2 ($\bar{P}_{12}$).

A Slater determinant satisfies the Pauli Exclusion Principle because if any two electrons had identical quantum numbers (including spin) then two rows in the determinant would be identical making it zero. Further, the Antisymmetry Principle is satisfied since interchaning two rows of a determinant (which corresponds to interchanging the coordinates of two electrons) only changes the sign of the determinant. Hence, Slater determinants are compatible with the Pauli Exclusion Principle and the Antisymmetry Principle.

3.4 Energy Expression for a Closed Shell Configuration [19]

Derivation of the Hartree-Fock equations requires the application of the Variational Principle to the energy of the molecular system. It is therefore necessary to have a convenient expression for this quantity in terms of the orbitals involved. For this, we will consider a closed-shell electronic system (that is one in which all occupied orbitals contain the maximum two electrons and which is therefore a singlet state). Analogous expressions for open-shell electronic systems (in which there is at least one unpaired electron) apply.

The Slater determinant given in (3.35) applies to a closed shell system containing 2n paired electrons. To find the normalization constant Π, the integrated probability density is set to unity and we use orthonormalized one electron orbitals. Hence

$$\int\Psi^*\Psi \, d\tau_1 d\tau_2 \ldots d\tau_{2n} = 1 \qquad (3.37)$$

and

$$S_{ij} = \int\psi_i^*(1)\,\psi_j(1)d\tau_1 = \delta_{ij} \qquad (3.38)$$

Using (3.35) in (3.37) and assuming, without loss of generality, only real wavefunctions yields

$$\Pi^2 \sum_{\bar{P}} \sum_{\bar{P}'} (-1)^P(-1)^{P'} \iint \bar{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}$$
$$\times\, \bar{P}'\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} = 1 \qquad (3.38a)$$

The integration is over spatial and spin coordinates of all electrons. Now [19] the multiple integral in this equation associated with any particular pair of permutation will be zero unless $\overline{P}$ and $\overline{P}'$ are identical. This follows from the orthogonality condition given by (3.38) since an integration 8 over any two spin orbitals which differ either in the spatial or spin function must be zero. Moreover when $\overline{P}$ and $\overline{P}'$ are identical the multiple integral is unity. Hence the summation on the left-hand side of (3.38a) is simply equal to the number of permutations of the 2n electrons. This number is (2n)! Hence

$$\Pi^2 (2n)! = 1 \qquad (3.39)$$

and

$$\Pi = [(2n)!]^{-\frac{1}{2}} \qquad (3.40)$$

The electronic Hamiltonian given by equation (3.2) consists of two one-electron terms and one two-electron term

$$H = H_1 + H_2 \qquad (3.41)$$

where the superscript "el" and the coordinates $\overline{r}_i$, $\overline{R}_k$ are understood and where H_1 is the one-electron term and H_2 the two electron term. From (3.2) we find

$$H_1 = \sum_p -\frac{1}{2}\overline{\nabla}_p^2 - \sum_p \sum_A Z_A \overline{r}_{pA}^{-1} \qquad (3.42)$$

and

$$H_2 = \sum_{p<q}\sum \overline{r}_{pq}^{-1} \qquad (3.43)$$

where

p is the number of electrons, Z_A is the charge on nucleus A and where atomic unit system units(in which the electronic charge and mass and the normalized Planck constant are all of unit magnitude) have been used.r_{pA} is the distance between the pth electron and the Ath nucleus and r_{pq} the distance between the pth and qth electrons. The core Hamiltonian $H^{core}(p)$ is defined from (3.42) to be

$$H^{core}(p) = -\frac{1}{2}\nabla_p^2 - \sum_A Z_A \bar{r}_{pA}^{-1} \qquad (3.44)$$

Hence

$$H_1 = \sum_p H^{core}(p) \qquad (3.45)$$

$H^{core}(p)$ is the one-electron Hamiltonian and corresponds to the motion of an electron in the field of the bare nuclei.

Using (3.41) the energy expectation value for a molecular system can be separated into one-electron and two-electron parts

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|H_1|\Psi\rangle + \langle\Psi|H_2|\Psi\rangle \qquad (3.46)$$

Using (3.45)

$$\langle\psi|H_1|\Psi\rangle = \sum_p^{2n} \langle\Psi|H^{core}(p)|\Psi\rangle \qquad (3.47)$$

where 2n is the total number of electrons in the closed-shell system being considered. Now since all 2n electrons are indistinguishable and are treated identically in the wavefunction Ψ

$$\langle\Psi|H_1|\Psi\rangle = 2n\langle\Psi|H^{core}(1)|\Psi\rangle \qquad (3.48)$$

Using (3.35) and (3.40) gives

$$\langle\Psi|H_1|\Psi\rangle = \frac{2n}{(2n)!} \sum_{\overline{P}} \sum_{\overline{P}'} (-1)^{P}(-1)^{P'} \int\int \overline{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}$$

$$\times\ H^{\text{core}}(1)\ \overline{P}'\{\psi(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} \qquad (3.49)$$

$$\langle\Psi|H_1|\Psi\rangle = [(2n-1)!]^{-1} \sum_{\overline{P}} \sum_{\overline{P}'} (-1)^{P}(-1)^{P'} \int\int \overline{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}$$

$$\times\ H^{\text{core}}(1)\overline{P}'\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} \qquad (3.50)$$

Carrying out the integration over electrons 2,3 ... 2n shows that all terms in which $\overline{P} \neq \overline{P}'$ must yield zero. This follows from the orthogonality condition expressed by (3.38). Hence only terms in which $\overline{P} = \overline{P}'$ survive and (3.50) now becomes

$$\langle\Psi|H_1|\Psi\rangle = [(2n-1)!]^{-1} \sum_{\overline{P}} \int\int \overline{P}\ \{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}$$

$$\times\ H^{\text{core}}(1)\ \overline{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} \qquad (3.51)$$

Integration over electrons 2,3, ... 2n gives unity in each term (again by 3.38). Summed over $\overline{P}$ this gives (2n-1)! Also H^{core} is spin independent, since spin-orbit interaction terms are not included in the Hamiltonian and integration over the spin coordinates of electron 1 yields a further factor of unity. Hence

$$\langle\Psi|H_1|\Psi\rangle = 2 \sum_{i=1}^{n} \int \psi_i(1)\ H^{\text{core}}(1)\psi_i(1)d\tau_1 \qquad (3.52)$$

where now the integration is over the spatial coordinates of electron 1 only and the factor of 2 with summation over n terms is a consequence of the fact that there are two electrons in each of the molecular orbitals ψ_i.

From (3.52) the expectation value of the one-electron core Hamiltonian is defined as

$$H_{ii} = \int \psi_i(1)\ H^{core}(1)\psi_i(1)d\tau_1 \qquad (3.53)$$

Hence

$$<\Psi|H_1|\Psi> = 2\sum_{i=1}^{n} H_{ii} \qquad (3.54)$$

The expectation value of the two electron term H_2 can be evaluated in a similar manner. For 2n electrons there are [2n(2n-1)/2] electron-electron repulsion terms because each pair contributes only once in the summation in (3.43). Furthermore, because of the indistinguishability of electrons, each will give the same contribution.

Hence

$$<\Psi|H_2|\Psi> = \frac{1}{2}(2n)(2n-1)<\Psi|r_{12}|\Psi> \qquad (3.55)$$

Using (3.35) and (3.40) yields

$$<\Psi|H_2|\Psi> = \frac{1}{2}(2n)(2n-1)[(2n)!]^{-1}\sum_{\bar{P}}\sum_{\bar{P}}(-1)^{P}(-1)^{P'}\int\int\bar{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots$$

$$\ldots\psi_n(2n)\beta(2n)\}r_{12}^{-1}\ P'\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} \qquad (3.56)$$

$$<\Psi|H_2|\Psi> = \frac{1}{2}[(2n-2)!]^{-1}\sum\sum_{\overline{PP'}}(-1)^{P}(-1)^{P'}\int\int\bar{P}\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}$$

$$\times\ r_{12}^{-1}\ P'\{\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\beta(2n)\}d\tau_1 d\tau_2\ldots d\tau_{2n} \qquad (3.57)$$

Once again, the orthogonality condition expressed by (3.38) leads to non zero terms if $\overline{P}$ and $\overline{P}'$ are identical. This time however, because of the two-electron term $\overline{r}_{12}$, a non zero result is also obtained when $\overline{P}'$ differs from $\overline{P}$ only by the interchange of electrons 1 and 2. These two cases will be considered separately.

Consider first the case when $\overline{P}$ and $\overline{P}'$ are identical. There are (2n-2)! permutations for each assignment of electrons 1 and 2 to any two molecular orbitals. This cancels with the $[(2n-2)!]^{-1}$ term in (3.57). If electrons 1 and 2 are assigned to different spatial molecular orbitals ψ_i and ψ_j both may have α or β spins leading to four terms of the form 1/2 J_{ij} where the factor 1/2 is left over from (3.57) and where

$$J_{ij} = \iint \psi_i(1)\psi_j(2) \frac{1}{r_{12}} \psi_i(1)\psi_j(2)d\tau_1 d\tau_2 \qquad (3.58)$$

There are four such terms because the case where electron 1 is in ψ_i and 2 is in ψ_j with both electrons having α spins or both electrons having β spins is identical to the case where electron 1 is in ψ_j and 2 in ψ_i with the same restriction on their spins.

If electrons 1 and 2 are assigned to the same molecular orbital then they must have opposite spins and this gives rise to two terms of the form $\frac{1}{2} J_{ii}$.

The total contribution is therefore

$$2\sum_{i=1}^{n}\sum_{j\neq i}^{n} J_{ij} + \sum_{i=1}^{n} J_{ii}$$

where the summations are over the n molecular orbitals. J_{ii} and J_{ij} are two-electron terms with the integration in (3.58) being over the six spatial coordinates of the two electrons. These terms are called the *Coulomb Integrals* and represent the Coulomb repulsion energy between two electrons residing in the region of overlap of the orbitals ψ_i and ψ_j assuming no electronic correlation (i.e. assuming that all electrons move independently in the orbitals to which they are assigned) [19,88].

Consider now the contribution to the energy (expectation) value when $\overline{P}'$ and $\overline{P}$ only differ from each other by an interchange of electrons 1 and 2.

If 1 and 2 are in spatially different molecular orbitals the following four possibilities exist:

Permutation $\overline{P}$	Permutation $\overline{P}'$
$\psi_i(1)\alpha(1)\ \psi_j(2)\alpha(2)$	$\psi_j(1)\alpha(1)\ \psi_i(2)\alpha(2)$
$\psi_i(1)\alpha(1)\ \psi_j(2)\beta(2)$	$\psi_j(1)\beta(1)\ \psi_i(2)\alpha(2)$
$\psi_i(1)\beta(1)\ \psi_j(2)\alpha(2)$	$\psi_j(1)\alpha(1)\ \psi_i(2)\beta(2)$
$\psi_i(1)\beta(1)\ \psi_j(2)\beta(2)$	$\psi_j(1)\beta(1)\ \psi_i(2)\beta(2)$

Here only the assignments of electrons 1 and 2 are shown since the other electrons must have the same assignments in both $\overline{P}$ and $\overline{P}'$ in order that a non-zero value result, as mentioned above.

Of these four sets, the second and third give vanishing terms by integration over the spin coordinates. The first and fourth each give $-\frac{1}{2}K_{ij}$ where

$$K_{ij} = \iint \psi_i(1)\psi_j(2)\,\frac{1}{r_{12}}\,\psi_j(1)\psi_i(2)\,d\tau_1 d\tau_2 \qquad (3.59)$$

The $\frac{1}{2}$ term arises as explained above for J_{ij}. The minus sign is a consequence of the fact that for these permutations $(-1)^P(-1)^{P'} = -1$, since these permutations can be derived from each other by a single interchange. In other words, if $\overline{P}$ is an even permutation then $\overline{P}'$ is an odd one and vice-versa. If electrons 1 and 2 are assigned to the same orbital then they must have opposite spins and the corresponding integral vanishes by integration over spin coordinates. K_{ij} is called the *Exchange Integral*. It is a six (spatial) dimensional two-electron integral like the Coulomb Integral. It reflects the energy stabilization due to the partial correlation of electrons of parallel spin [19].

The final expression for the electronic energy of the system then becomes

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|H_1+H_2|\Psi\rangle \equiv E^{el} = 2\sum_i^n H_{ii} + \sum_i^n J_{ii} + \sum_i^n \sum_{j\neq i}^n (2J_{ij}-K_{ij}) \quad (3.60)$$

where E^{el} is the total electronic energy of the system as given by the eigenvalue of the Schroedinger electronic waveequation (3.1). The last equality in (3.60) of course only holds under the stipulations of the orbital and other approximations (e.g. the Born-Oppenheimer Approximation) made.

From (3.58) and (3.59) it follows

$$K_{ii} = J_{ii} \quad (3.61)$$

Using (3.61) equation (3.60) may be rewritten then as

$$E^{el} = 2\sum_i H_{ii} + \sum_i J_{ii} + \sum_i^n \sum_{j\neq i}^n (2J_{ij}-K_{ij}) + \sum_i J_{ii} - \sum_i K_{ij}$$

$$E^{el} = 2\sum_i H_{ii} + \sum_i^n \sum_j^n (2J_{ij} - K_{ij}) \quad (3.62)$$

H_{ii} is a one electron integral which represents the energy of an electron in a molecular orbital ψ_i in the field of the bare nuclei, and this is multiplied by 2 since there are two electrons in each orbital. J_{ij}, the Coulomb Integral, is a two-electron integral which represents the Coulomb repulsion energy of two electrons in the overlap region of orbitals ψ_i and ψ_j. K_{ij}, the Exchange Integral enters with a negative sign in the energy expression because it represents the stabilization energy of interaction between electrons with parallel spins in different orbitals ψ_i and ψ_j. (We note that the second and third permutations in the set which accounts for K_{ij} have electrons with antiparallel spins and these give a vanishing value).

One-electron energies can now be defined as

$$E_i = H_{ii} + \sum_{j}^{n} (2J_{ij} - K_{ij}) \tag{3.63}$$

E_i is the energy of an electron in the molecular orbital ψ_i interacting with the nuclei and the other (2n-1) electrons.

From (3.62) and (3.61) it follows that

$$E^{el} = \sum_{i}^{n} (E_i + H_{ii}) \tag{3.64}$$

Also from (3.63)

$$2\sum_{i=1}^{n} E_i = 2\sum_{i=1}^{n} H_{ii} + 2\sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij})$$

$$2\sum_{i=1}^{n} E_i = 2\sum_{i=1}^{n} H_{ii} + \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij}) + \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij})$$

and using (3.62) this becomes

$$2\sum_{i=1}^{n} E_i = E^{el} + \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij})$$

therefore

$$E^{el} = 2\sum_{i=1}^{n} E_i - \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij}) \tag{3.65}$$

Equations (3.60) to (3.65) are forms that are useful in deriving the Hartree-Fock Equations after application of the Variational Principle.

3.5 The Hartree-Fock Equations [19,92,95]

The energy expression derived above for a closed shell system can be used to derive a set of differential equations for the optimum forms of the molecular orbitals by use of the Variational Principle [17,19]. According to this principle, an approximate wavefunction describing a system is an upper bound on the exact ground-state energy and the closer the trial wavefunction is to the exact wavefunction the closer the approximate energy will be to the exact energy. The optimum wavefunction is then that which corresponds to the minimum in energy as obtained by varying the trial wavefunction with respect to variational parameters included in, or inherent to, the approximate wavefunction. The best choice for a trial wavefunction is, therefore, one which is the least constrained and contains enough variational parameters to yield the required amount of accuracy after application of the Variational Principle.

The molecular orbital wavefunctions used to derive the energy expressions (3.60) to (3.65) above are fairly flexible, the only approximations made in deriving them being the Born-Oppenheimer Approximation, the Orbital Approximation and the orthonormalization of the individual molecular orbitals (3.38). The first of these approximations is generally extremely powerful, only breaking down under exceptional circumstances such as near regions of curve crossing [68-72]. The remaining two constraints are not seriously inhibiting factors either. Semiemperical methods such as CNDO and CNDO/S which are based on the Hartree-Fock equations have the added flexibility, to reduce the effects of any approximations made, of semi-emperical parameterization.

The procedure is therefore to minimize the energy expectation value $<\Psi|H|\Psi>$ where Ψ is the many electron wavefunction described above (see equations 3.35 and 3.60 to 3.65). This is done by using the method of undetermined multipliers [19].

A function G is first defined as follows

$$G = E - 2 \sum_{i}^{n} \sum_{j}^{n} E_{ij} S_{ij} \qquad (3.66)$$

where E corresponds to E^{el} with the subscript dropped for convenience, E_{ij} are the as yet undetermined multipliers and S_{ij} are the overlaps defined by (3.38). Using (3.62) in (3.66) results in

$$G = 2 \sum_{i}^{n} H_{ii} + \sum_{i}^{n} \sum_{j}^{n} (2J_{ij} - K_{ij}) - 2 \sum_{i}^{n} \sum_{j}^{n} E_{ij} \quad S_{ij} \qquad (3.67)$$

A stationary point of the function G is such that the variation, δG, in G as a consequence of varying all orbitals ψ_i by an infinitesimal amount to $\psi_i + \delta\psi_i$, is zero. The variation in G, δG, can be written as

$$\delta G = 2 \sum_{i} \delta\ H_{ii} + \sum_{ij}\sum(2\delta J_{ij} - \delta K_{ij}) - 2 \sum_{ij}\sum E_{ij}\delta S_{ij} \qquad (3.68)$$

where from equations (3.53), (3.58), (3.59) and (3.38)

$$\delta H_{ii} = \int \delta\psi_i(1) H^{core}(1) \psi_i(1) d\tau_1 \qquad (3.69)$$

$$\delta J_{ij} = \int \delta\psi_i(1) (\int \psi_j(2) \frac{1}{r_{12}} \psi_j(2) d\tau_2) \psi_i(1) d\tau_1$$

$$+ \int \delta\psi_j(2) (\int \psi_i(1) \frac{1}{r_{12}} \psi_i(1) d\tau_1) \psi_j(2) d\tau_2 \qquad (3.70)$$

$$\delta K_{ij} = \int \delta\psi_i(1) (\int \psi_j(2) \frac{1}{r_{12}} \psi_i(2) d\tau_2) \psi_j(1) d\tau_1$$

$$+ \int \delta\psi_j(2) (\int \psi_i(1) \frac{1}{r_{12}} \psi_j(1) d\tau_1) \psi_i(2) d\tau_2 \qquad (3.71)$$

and $$\delta S_{ij} = \int \delta\psi_i(1) \psi_j(1) d\tau_1 \qquad (3.72)$$

Since electrons 1 and 2 are indistinguishable the terms on the right-hand sides of (3.70) and (3.71) can be rewritten to give

$$\delta J_{ij} = \int \delta\psi_i(1)\left(\int \psi_j(2)\,\frac{1}{r_{12}}\,\psi_j(2)\delta\tau_2\right)\psi_i(1)\delta\tau_1$$

$$+ \int \delta\psi_j(1)\left(\int \psi_i(2)\,\frac{1}{r_{12}}\,\psi_i(2)\delta\tau_2\right)\psi_j(1)\delta\tau_1 \qquad (3.73)$$

$$\delta K_{ij} = \int \delta\psi_i(1)\left(\int \psi_j(2)\,\frac{1}{r_{12}}\,\psi_1(2)\delta\tau_2\right)\psi_i(1)d\tau_1$$

$$+ \int \delta\psi_j(1)\left(\int \psi_i(2)\,\frac{1}{r_{12}}\,\psi_j(2)\delta\tau_2\right)\psi_1(1)\delta\tau_1 \qquad (3.74)$$

Defining the Coulomb operator, J_j, as

$$J_j(1) = \int \psi_j(2)\,\frac{1}{r_{12}}\,\psi_j(2)\delta\tau_2 \qquad (3.75)$$

and an Exchange operator, K_j, as

$$K_j(1)\psi_i(1) = \left(\int \psi_j(2)\,\frac{1}{r_{12}}\,\psi_i(2)\delta\tau_2\right)\psi_j(1) \qquad (3.76)$$

equations (3.73) and (3.75) can be rewritten as

$$\delta J_{ij} = \int \delta\psi_i(1)J_j(1)\psi_i(1)\delta\tau_1 + \int \delta\psi_j(1)J_i(1)\psi_j(1)\delta\tau_1 \qquad (3.77)$$

$$\delta K_{ij} = \int \delta\psi_i(1)K_j(1)\psi_i(1)\delta\tau_1 + \int \delta\psi_j(1)K_i(1)\psi_j(1)\delta\tau_1 \qquad (3.78)$$

From (3.68), (3.69), (3.77) and (3.78)

$$\delta G=2\sum_{i}\int\delta\psi_{i}(1)H^{\text{core}}(1)\psi_{i}(1)\delta\tau_{1}+\sum_{i}\sum_{j}2\int\delta\psi_{i}(1)J_{j}(1)\psi_{i}(1)\delta\tau_{1}+\sum_{i}\sum_{j}2\int\delta\psi_{j}(1)J_{i}(1)\psi_{j}(1)\delta\tau_{1}$$

$$-\sum_{i}\sum_{j}\int\delta\psi_{i}(1)K_{j}(1)\psi_{i}(1)\delta\tau_{1}-\sum_{i}\sum_{j}\int\delta\psi_{j}(1)K_{i}(1)\psi_{j}(1)\delta\tau_{1}-2\sum_{i}\sum_{j}E_{ij}\int\delta\psi_{i}(1)\psi_{j}(1)\delta\tau_{1} \tag{3.79}$$

Once again, because electrons 1 and 2 are indistinguishable the third term in (3.79) is equal to the second and the fifth equal to the fourth. Hence

$$\delta G=2\sum_{i}\int\delta\psi_{i}(1)[H^{\text{core}}(1)\psi_{i}(1)+\sum_{j}(2J_{j}(1)-K_{j}(1))\psi_{i}(1)-\sum_{j}E_{ij}\psi_{j}(1)]\delta\tau_{1} \tag{3.80}$$

This expression holds for any electron and since the increment $\delta\psi_i$ is arbitrary the requirement of the Variational Principle that δG be zero leads immediately to

$$[H^{\text{core}} + \sum_{j}(2J_{j} - K_{j})]\psi_{i} = \sum_{j} E_{ij}\,\psi_{j} \tag{3.81}$$

where

$i = 1, 2, \ldots n$

and

$j - 1, 2, \ldots n.$

Defining the Fock Hamiltonian, F, as

$$F \equiv H^{\text{core}} + \sum_{j} 2J_{j} - K_{j} \tag{3.82}$$

leads to

$$F\psi_{i} = \sum_{j} E_{ij}\psi_{j} \quad i=1,\ldots\ldots n;\ j=1,\ldots\ldots n \tag{3.83}$$

Equation (3.83) represents a set of differential equations each with an eigenvalue E_{ij}. The reason for the summation in(3.83)is that several basis sets could be chosen for the same electronic wavefunction. Since the elements E_{ij} form a Hermitian matrix [19] there exists a unitary transformation [17] which will diagonalize this matrix. Applying such a transformation the set in (3.83) can be reduced [19] to a standard eigenvalue problem.

$$F\psi_i = E_i\psi_i \quad i=1,2......n \tag{3.84}$$

These equations are commonly called the Hartree-Fock Equations.

3.6 The Roothaan Equations [19,96]

The molecular orbitals ψ_i above are spatially delocalized over all the atoms in the molecule. It is necessary in the solution of the Hartree-Fock equations, for example by the Self Consistent Field (SCF) Method described below, to start with an approximate form of the molecular orbitals. The most widely used technique is to approximate each molecular orbital ψ_i, with a Linear Combination of Atomic Orbitals (LCAO) of the atoms of the molecular system. This method has the advantage that the contribution of each of the constituent atom to the electronic properties of the molecule can be discerned relatively easily.

Molecular orbitals may be specified in terms of the atomic electronic functions as basis sets. Three types of basis sets that are most frequently encountered in theoretical chemistry are: (1) Valence basis sets (2) Minimal basis sets and (3) Extended basis sets. A valence basis set is the set of all the valence orbitals of all the atoms in the molecular system. A minimal basis set is a set which includes the valence basis set plus all the inner orbitals of all the atoms. An extended basis set comprises of the minimal basis set plus any number of atomic orbitals lying outside the valence shell of each atom. For instance for the HF molécule the valence basis set would be the hydrogen 1s orbital function plus the 2s, $2p_x$, $2p_y$ and $2p_z$ orbital wavefunctions of the fluorine atom. Addition of the fluorine atomic 1s orbital function to this set makes it a minimal basis set. Addition of any of the other atomic orbital functions such as the hydrogen 2s, 2p, 3s, 3p, 3d... and/or the fluorine 3s, 3p, 3d, 4s..., would make the minimal basis set an extended set. CNDO/1, CNDO/2 CNDO/S and other derivatives of CNDO for calculating electronic states use valence basis sets.

The molecular orbitals ψ_i are written as LCAO-MO's as follows

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu} \qquad (3.85)$$

where ϕ_{μ} are atomic valence orbital real functions. The summation is over the basis set of atomic orbital functions.

The requirement that molecular orbitals be orthonormal, as expressed by (3.38), leads to

$$\sum_{\mu\nu}\sum c^{*}_{\mu i}\, c_{\nu j} \cdot S_{\mu\nu} = \delta_{ij} = S_{ij} \qquad (3.86)$$

where

$$S_{\mu\nu} = \int \phi_{\mu}(1)\phi_{\nu}(1)d\tau_1 \qquad (3.87)$$

is the atomic overlap integral.

For a closed shell system containing 2n electrons

$$2n = 2\int \sum_{i}^{occ} \psi_i(1)\psi_i(1)d\tau_1 \qquad (3.88)$$

Hence

$$2n = 2\int \sum_{i}^{occ} \sum_{\mu} \sum_{\nu} c^{*}_{\mu i}\, c_{\nu i}\, \phi_\mu \phi_\nu dR \qquad (3.89)$$

where (3.85) has been used.

Defining the density matrix $P_{\mu\nu}$ as

$$P_{\mu\nu} = 2 \sum_{i}^{occ} c^{*}_{\mu i}\, c_{\nu i} \qquad (3.90)$$

yields the following equation

$$2n = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \int\phi_\mu(1)\phi_\nu(1)d\tau_1 = \sum_{\mu\nu} P_{\mu\nu}\, S_{\mu\nu} \qquad (3.91)$$

Substituting (3.85) into (3.53) yields

$$H_{ii} = \int \sum_{\mu} \sum_{\nu} c^{*}_{\mu i}\, \phi_\mu(1)\, H^{core}(1)\, c_{\nu i}\phi_\nu(1)d\tau_1 \qquad (3.92)$$

Defining

$$H_{\mu\nu} = \int\phi_\mu(1)\, H^{core}(1)\, \phi_\nu(1)d\tau_1 \qquad (3.93)$$

and substituting into (3.92) gives

$$H_{ii} = \sum_{\mu\nu}\sum c^{*}_{\mu i}\, c_{\nu i}\, H_{\mu\nu} \qquad (3.94)$$

This is an expression for the expectation value of the one-electron core Hamiltonian of the system in terms of the atomic basis functions.

In order to derive analogous expressions for the Coulomb and Exchange Integrals given by (3.58) and (3.59) we write the following molecular orbitals (following (3.85)

$$\psi_i(1) = \sum_{\nu} c_{\nu i}\ \phi_{\nu}(1) \tag{3.95}$$

$$\psi_i^*(1) = \sum_{\mu} c_{\mu i}^*\ \phi_{\mu}^*(1) \tag{3.96}$$

$$\psi_j(2) = \sum_{\sigma} c_{\sigma j}\ \phi_{\sigma}(2) \tag{3.97}$$

$$\psi_j^*(2) = \sum_{\lambda} c_{\lambda j}^*\ \phi_{\lambda}^*(2) \tag{3.98}$$

Further, following (3.90) we write the atomic density matrix $P_{\lambda\sigma}$ as

$$P_{\lambda\sigma} = 2\sum_{j}^{occ} c_{\lambda j}^*\ c_{\sigma j} \tag{3.99}$$

Then, substituting (3.95) to (3.98) into (3.58) (with complex conjugation of the wavefunctions reintroduced for convenience),

$$J_{ij} = \iint \sum_{\sigma\nu\lambda\mu}\sum\sum\sum c_{\mu i}^*\phi_{\mu}^*(1)c_{\lambda j}^*\phi_{\lambda}^*(2)\ \frac{1}{r_{12}}\ c_{\nu i}\phi_{\nu}(1)c_{\sigma j}\phi_{\sigma}(2)d\tau_1 d\tau_2 \tag{3.100}$$

$$J_{ij} = \sum_{\mu\lambda\nu\sigma} c_{\mu i}^* c_{\lambda j}^* c_{\nu i} c_{\sigma j} \iint \phi_{u}^*(1)\phi_{\nu}(1)\ \frac{1}{r_{12}}\ \phi_{\lambda}^*(2)\phi_{\sigma}(2)d\tau_1 d\tau_2 \tag{3.101}$$

Hence

$$J_{ij} = \sum_{\mu\lambda\nu\sigma} c_{\mu i}^*\ c_{\lambda j}^*\ c_{\nu i}\ c_{\sigma j}(\mu\nu/\lambda\sigma) \tag{3.102}$$

where, by definition, $(\mu\nu/\lambda\sigma)$ is a two electron six dimensional integral given by

$$(\mu\nu/\lambda\sigma) = \iint \phi_{\mu}^*(1)\phi_{\nu}(1)\ \frac{1}{r_{12}}\ \phi_{\lambda}^*(2)\phi_{\alpha}(2)d\tau_1 d\tau_2 \tag{3.103}$$

Similarly the two electron six dimensional Exchange Integral given by (3.59) becomes

$$K_{ij} = \sum_{\mu\lambda\nu\sigma} c^*_{\mu i}\, c^*_{\lambda j}\, c_{\nu i}\, c_{\sigma j} (\mu\lambda/\nu\sigma) \qquad (3.104)$$

In order to derive the total electronic energy as given by (3.62) in terms of the atomic basis functions, the core Hamiltonian has to be summed over i, and the two electron integrals have to be summed over i and j.

From (3.94)

$$\sum_i H_{ii} = \sum_i \sum_{\mu\nu} c^*_{\mu i}\, c_{\nu i}\, H_{\mu\nu} \qquad (3.105)$$

Using (3.90) yields

$$2 \sum_i H_{ii} = \sum_{\mu\nu} P_{\mu\nu}\, H_{\mu\nu} \qquad (3.106)$$

Similarly

$$\sum_i \sum_j J_{ij} = \sum_i \sum_j \sum_{\mu\lambda\nu\sigma} c^*_{\mu i}\, c^*_{\lambda j}\, c_{\nu i}\, c_{\sigma j}\, (\mu\nu/\lambda\sigma) \qquad (3.107)$$

Using (3.90) and (3.99) results in

$$2 \sum_i \sum_j J_{ij} = \frac{1}{2} \sum_{\mu\lambda\nu\sigma} P_{\mu\nu}\, P_{\lambda\sigma}\, (\mu\nu/\lambda\sigma) \qquad (3.108)$$

Similarly

$$\sum_i \sum_j K_{ij} = \frac{1}{4} \sum_{\mu\lambda\nu\sigma} P_{\mu\nu}\, P_{\lambda\sigma}\, (\mu\lambda/\nu\sigma) \qquad (3.109)$$

Substituting (3.106), (3.108) and (3.109) into (3.62) yields

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\lambda\nu\sigma} P_{\mu\nu} P_{\lambda\sigma} \left[(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\nu\sigma)\right] \tag{3.110}$$

Substituting (3.110) into (3.66) and utilizing the stationary point condition $\delta G=0$ yields

$$\delta \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \delta \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left[(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\nu\sigma)\right] - 2\delta \sum_{ij}\sum E_{ij} S_{ij} = 0 \tag{3.111}$$

Substituting equations (3.90), (3.99) and (3.86) into (3.111)

$$2 \sum_{i\mu\nu}\sum \delta c^{*}_{\mu i} c_{\nu i} H_{\mu\nu} + \sum_{ij} \sum_{\mu\nu\lambda\sigma} (\delta c^{*}_{\mu i} c_{\nu i} c^{*}_{\lambda j} c_{\sigma j})[2(\mu\nu/\lambda\sigma) - (\mu\lambda/\nu\sigma)] - 2 \sum_{ij\mu\nu}\sum \delta c^{*}_{\mu i} E_{ij} c_{\nu j} S_{\mu\nu} = 0 \tag{3.112}$$

Minimizing with respect to $c^{*}_{\mu i}$ and eliminating the common summations over i and μ results in

$$\sum_{\nu} 2H_{\mu\nu} c_{\nu i} + \sum_{j} \sum_{\nu\lambda\sigma} c^{*}_{\lambda j} c_{\sigma j} c_{\nu i} [2(\mu\nu/\lambda\sigma) - (\mu\lambda/\nu\sigma)] = 2 \sum_{j} E_{ij} \sum_{\nu} c_{\nu j} S_{\mu\nu} \tag{3.113}$$

As before, it can be shown that there exists a unitary transformation which when applied to the basis orbitals diagonalizes the matrix E_{ij} [19]. Performing this transformation results in

$$E_{ij} = 0 \quad i \neq j \tag{3.114}$$

$$E_{ij} = E_i \quad i = j \tag{3.115}$$

Hence

$$\sum_{\nu}\{2H_{\mu\nu}c_{\nu i}+\sum_{\lambda\sigma j}\sum c^{*}_{\lambda j}\, c_{\sigma j}\, c_{\nu i}[2(\mu\nu/\lambda\sigma)-(\mu\lambda/\nu\sigma)]\} = 2\sum_{i} E_{i}\sum_{\nu} c_{\nu i}\, S_{\mu\nu}$$

Using (3.99) this becomes

$$\sum_{\nu}\{H_{\mu\nu}+\sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\nu\sigma)]\}\, c_{\nu i} - E_{i}\sum_{\nu} c_{\nu i}\, S_{\mu\nu} = 0 \qquad (3.116)$$

Defining

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu/\lambda\sigma) - \frac{1}{2}\,(\mu\lambda/\nu\sigma)] \qquad (3.117)$$

equation (3.116) can be written in the form

$$\sum_{\nu}(F_{\mu\nu} - E_{i}S_{\mu\nu})\, c_{\nu i} = 0 \qquad (3.118)$$

These are the Roothaan Equations.

3.7 Complete Neglect of Differential Overlap Methods [18,19,88]

CNDO methods are a particular set of semiemperical techniques. These methods ignore certain differential overlap(defined below) integrals and approximate other difficult ones by using experimental data. There are several general characteristics that must be satisfied by approximate m.o. (including CNDO) methods. Hence to be useful, firstly the methods should be simple enough to be applicable to moderately large molecules or molecular complexes without becoming prohibitively expensive in terms of computational time. Secondly, the approximations made should be accurate enough to describe the general physical and chemical properties of the molecular system. Thirdly, the theory should be developed in such a way that the results can be interpreted in detail and used to support or discount different hypotheses of the physical and chemical pictures that may be available for a property or properties of a molecule or molecular complex. In this respect, approximate semiemperical methods can often be interpreted more usefully than complex methods which yield mathematically accurate wavefunctions. Finally, a theory which attempts to explain the electronic properties of a molecule must be sufficiently general to take account of all the "active" electrons. Generally this means all the valence electrons. Hence the usefulness of a molecular orbital theory is increased greatly by an explicit provision for σ as well as π valence electrons. The extension of quantum mechanical techniques to *all* the valence electrons of a molecule must remain a major objective. The CNDO methods to be described here attempt to remain faithful to these objectives.

The differential overlap between two atomic functions ϕ_μ and ϕ_ν is defined as the probability of finding an electron i in a volume common to the two functions. This probability is proportional to the following differential overlap integral [88]

$$S_{\mu\nu} = \int \phi_\mu(i)\ \phi_\nu(i)\ d\tau_i \tag{3.119}$$

where $\phi_\mu(i)$ and $\phi_\nu(i)$ are atomic orbitals. The Zero Differential Overlap (ZDO) or the Neglect of Differential Overlap (NDO) Approximation is expressed by

$$S_{\mu\nu} = \int\phi_\mu(i)\phi_\nu(i)d\tau_i = \delta_{\mu\nu} \tag{3.120}$$

Strict NDO therefore implies a vanishing value for the overlap integral of all nonidentical atomic orbitals. We note here that equation (3.120) is very restrictive quite unlike the orthornormalization of the molecular orbitals expressed by equation (3.38). Equation (3.120) is a drastic approximation for, although $S_{\mu\nu}$ will be equal to unity if normalized atomic orbitals are used, it is known [77] that $S_{\mu\nu}$ for adjacent centres is of the order of 0.25 for 2p overlap, a value certainly far from zero. The only real justification for the NDO Approximation is that it greatly simplifies computation. The Basic Huckel Molecular Orbital Theory is the strictest application of the NDO Approximation [61,77], but even it retains non-zero values for $S_{\mu\nu}$ if ϕ_μ and ϕ_ν are on adjacent atoms. CNDO and INDO (Intermediate Neglect of Differential Overlap) methods also utilize (3.120) but somewhat more cautiously. At several places in the formulation of these theories experimental data is used to include parameters which tend to compensate for the approximations made, the large number of possible options partly accounting for the numerous CNDO and INDO parameterization methods. Only wise use of "emperical experience" [18] leads to useful theories. Nonetheless, it is truly remarkable that calculations incorporating the NDO Approximation have been so successful, especially when, clearly, this approximation is fundamentally at variance with the principle of maximum overlap in chemical bonding [77].

The consequences of the NDO Approximation are given below for the major types of integrals encountered [88].

(a) Overlap Integral: By definition of NDO

$$S_{\mu\nu} = \int \phi_\mu(1)\, \phi_\nu(1)d\tau_1 = \delta_{\mu\nu} \qquad (3.121)$$

(b) Nuclear-Electron Attraction Integrals

$$Z_k \int \frac{\phi_\mu(1)\phi_\nu(1)d\tau_1}{r} = 0 \text{ unless } \mu=\nu \qquad (3.122)$$

(c) Two Electron Integrals

$$\iint \phi_\mu(1)\phi_\nu(1)\, \frac{1}{r_{12}}\, \phi_\lambda(2)\phi_\sigma(2)d\tau_1 d\tau_2 = (\mu\nu/\lambda\sigma) = (\mu\mu/\lambda\lambda)\, \delta_{\mu\nu}\delta_{\lambda\sigma} \qquad (3.123)$$

These results (with appropriate qualifications to be described later), are used in CNDO. However, before this is done it is important to check if the NDO Approximation is invariant to rotational transformations. If it is not then additional approximations must be made to restore such invariance [19]. Invariance to rotation is necessary because clearly whatever approximations are invoked in developing an m.o. theory it is essential that the theory yield the same results regardless of the choice of the coordinate axis.

To see if the NDO Approximation is invariant to rotation consider for example [19] a rotation of 45° about the z axis. The new axes x' and y' are then related to the initial ones, x and y, in the following manner.

$$x' = (x + y)/\sqrt{2} \tag{3.124}$$

$$y' = (-x + y)/\sqrt{2} \tag{3.125}$$

Consider the product of a 2 p_x and a 2 p_y atomic orbital. This product is proportional to the product xy. Under transformations (3.124) and (3.125) the product becomes

$$x'y' = \frac{1}{2}\,(y^2 - x^2) \tag{3.126}$$

It follows then [19] that the differential overlap $\phi_\mu\phi_\nu$ in the new axis can be written in terms of the old axis as

$$(2p_{x'})(2p_{y'}) = \frac{1}{2}\,[(2p_y)^2 - (2p_x)^2] \tag{3.127}$$

Hence, the neglect of differential overlap in one coordinate system is not equivalent to the same approximation in the other coordinate system, unless the righthand side of (3.127) is neglected too.

It can be shown [19] that rotational invariance is restored if the additional approximation of making two-electron integrals depend only on the nature of the atoms A and B to which ϕ_μ and ϕ_ν belong is made. Hence, if the additional qualification

$$(\mu\mu/\lambda\lambda) = \gamma_{AB} \left\{ \begin{array}{l} \text{for all } \mu \text{ on atom A} \\ \text{and} \\ \text{for all } \lambda \text{ on atom B} \end{array} \right. \qquad (3.128)$$

is made, then as Pople and Beveridge [19] show, the NDO Approximation is invariant to rotation. γ_{AB} is then an average electrostatic repulsion between any valence electron on A and any valence electron on B. For two electrons on the same atom the integral is again made dependent only on the nature of the atom and not upon the nature of the orbitals involved [88]. Hence,

$$(\mu\mu/\mu\mu) = \gamma_{AA} \text{ for all } \mu \text{ on atom A} \qquad (3.129)$$

From (3.123) and this additional simplification it follows that

$$\int\int\phi_\mu(1)\phi_2(1)\frac{1}{r_{12}}\,\phi_\lambda(2)\phi_\sigma(2)d\tau_1 d\tau_2 = (\mu\mu/\lambda\lambda) = \gamma_{AB} \left\{ \begin{array}{l} \text{for all } \mu \text{ on atom A} \\ \text{and} \\ \text{for all } \lambda \text{ on atom B} \end{array} \right. \qquad (3.130)$$

$$= (\mu\mu/\mu\mu) = \gamma_{AA} \text{ for all } \mu \text{ on atom A}$$

We note here that the NDO approximation, through equation (3.123) implies automatic neglect of all three and four centre two electron integrals. (If all the atomic orbitals $\phi_\mu, \phi_\nu, \phi_\lambda, \phi_\sigma$ belong to one atom then (3.123) is a one-centre two electron integral. If these orbitals belong to two different atoms, then (3.123) is a two-centre two electron integral. Similarly (3.123) is a three or four centre two electron integral depending on whether the atomic orbitals belong to three or four different atoms respectively).

If the Zero Differential Overlap is used for all atomic orbital pairs then equation (3.118), the Roothaan equation for the LCAO coefficients simplifies to

$$\sum_{\nu} F_{\mu\nu}\, c_{\nu i} = E_i\, c_{\mu i} \tag{3.131}$$

From (3.117) when $\mu=\nu$

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\mu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\mu\sigma)]$$

Using (3.123) $(\mu\lambda/\mu\sigma)$ is non-zero only when $\mu=\lambda$, $\mu=\sigma$. Hence $\mu=\nu=\lambda=\sigma$ and

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu}(\mu\mu/\mu\mu) + \sum_{\lambda} P_{\lambda\lambda}(\mu\mu/\lambda\lambda) \tag{3.132}$$

When $\mu\neq\nu$ $(\mu\nu/\lambda\sigma) = 0$, hence from (3.117)

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu}(\mu\mu/\nu\nu) \tag{3.133}$$

Substituting (3.128) and (3.129) in equations (3.132) and (3.133) we obtain

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu}\gamma_{AA} + \sum_{\lambda} P_{\lambda\lambda}\, \gamma_{AB} \quad \begin{array}{l} \phi_\mu \text{ on atom A} \\ \\ \phi_\lambda \text{ on atom B} \end{array} \tag{3.134}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu}\gamma_{AB} \quad \begin{array}{l} \phi_\mu \text{ on atom A} \\ \\ \phi_\nu \text{ on atom B} \end{array} \tag{3.135}$$

Defining

$$\sum_{\lambda} P_{\lambda\lambda} = \sum_{B} P_{BB} \quad \phi_\lambda \text{ on B} \tag{3.136}$$

yields, from (3.134)

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu}\gamma_{AA} + \sum_{B} P_{BB}\, \gamma_{AB}(\phi_\mu \text{ on atom A}) \tag{3.137}$$

P_{BB} is the symbol for the total electron density associated with atom B.

From (3.44) the core Hamiltonian operator becomes

$$H = -\frac{1}{2}\nabla^2 - \sum_B V_B \qquad (3.138)$$

where now $-V_B$ is the potential due to the nucleus plus the inner shells of atom B. (This is in contrast to the $H^{\text{core}}(p)$ defined by (3.44) in which the field considered is that of bare nuclei. Since in the CNDO Approximation only the valence electrons are treated explicitly the inner shell electrons potential field is included with that of the bare nuclei).

The diagonal matrix elements $H_{\mu\mu}$ are then given by

$$H_{\mu\mu} = \langle\mu| -\frac{1}{2}\nabla^2 - V_A - \sum_{B\neq A} V_B|\mu\rangle \qquad (3.139)$$

Hence

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} \langle\mu|V_B|\mu\rangle \qquad (3.140)$$

where

$$U_{\mu\mu} = \langle\mu| -\frac{1}{2}\nabla^2 - V_A|\mu\rangle \qquad (3.141)$$

ϕ_μ being on atom A. $U_{\mu\mu}$ is a one centre term and is essentially an atomic quantity being equal to the energy (kinetic plus potential) of the electron in orbital ϕ_μ in the field of the core of its own atom. The remaining terms in (3.140) are two centre terms giving the interaction of an electron in the valence orbital ϕ_μ of atom A with the cores (nuclei plus inner shells) of other atoms (collectively termed B). The off-diagonal core Hamiltonian matrix elements $H_{\mu\nu}$ can be divided into two groups. The first group involves different atomic orbitals ϕ_μ and ϕ_ν on the same atom A. The second group consists of terms involving ϕ_μ on atom A and ϕ_ν on another atom B.

Consider first the case where ϕ_μ and ϕ_ν are on the same atom A. As above the matrix elements $H_{\mu\nu}$ can be separated into two parts

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B \neq A} \langle\mu|V_B|\nu\rangle \quad \phi_\mu \phi_\nu \text{ on A} \tag{3.142}$$

This is analogous to equation (3.140) above, the first term being a one-centre term, the second being a set of two centre terms. In the CNDO Approximation, the valence orbitals on one atom are assumed to be indistinguishable. Hence, the interaction energy of any valence electron on atom A with the core (nuclei plus inner shell electrons) of any atom B, $\langle\mu|V_B|\mu\rangle$, is defined as [19]

$$\langle\mu|V_B|\mu\rangle = V_{AB} \text{ for all } \phi_\mu \text{ on A}$$

In CNDO neglect of monatomic (ϕ_μ,ϕ_ν both on atom A) differential overlap is extended to include the condition

$$\langle\mu|V_B|\nu\rangle = 0 \quad \phi_\mu,\phi_\nu \text{ both on atom A} \tag{3.143}$$

Now since ϕ_μ,ϕ_ν are functions of the s,p,d... type and ϕ_μ and ϕ_ν are not identical in equation (3.142) although they are both on atom A, it can be shown that symmetry arguments require that $U_{\mu\nu} = 0$ [19]. Hence from (3.142)

$$H_{\mu\nu} = 0 \quad \phi_\mu \neq \phi_\nu, \text{ both on atom A} \tag{3.144}$$

Using (3.142) in (3.140) yields

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} V_{AB} \quad \phi_\mu \text{ on A} \tag{3.145}$$

It remains now to find an expression for the off-diagonal core matrix elements $H_{\mu\nu}$ with ϕ_μ and ϕ_ν on different atoms A and B. In CNDO, differential overlap is not neglected here since these elements take account of the basic bonding capacity of the overlap between the orbitals. In other words, in CNDO diatomic differential overlap is not neglected although monatomic differential overlap is [19]. Separating the cores of atoms A and B, the off diagonal matrix elements are written as

$$H_{\mu\nu} = \langle\mu| - \frac{1}{2}\nabla^2 - V_A - V_B|\nu\rangle - \sum_{C(\neq A,B)} \langle\mu|V_C|\nu\rangle \quad \phi_\mu \text{ on A, } \phi_\nu \text{ on B} \tag{3.146}$$

where the second term represents the interaction energy of orbitals ϕ_μ and ϕ_ν with the cores of third atoms (besides A and B) C. In CNDO these integrals are neglected since they are comparable [19] to the three- and four-centre two-electron integrals which, as pointed out above, have already been ignored. The first term in equation (3.146) is a function of the local environment (namely the fields of the atoms A and B to which ϕ_μ and ϕ_ν belong) and is hence a measure of the lowering of energy levels as a consequence of an electron being in the electrostatic fields of two atoms simultaneously. Analogously to the integrals, β_0 and β_1, in Mulliken's CT theory (described in Chapter II), this term is called a *resonance integral* and is denoted by $\beta_{\mu\nu}$. Hence equation (3.146) becomes

$$H_{\mu\nu} = \beta_{\mu\nu} \quad \phi_\mu \text{ on A, } \phi_\nu \text{ on B} \tag{3.147}$$

CNDO now makes an assumption which is the result of "emperical experience" [18]. $\beta_{\mu\nu}$ is assumed to be proportional to $S_{\mu\nu}$, the differential overlap integral. It has been found necessary to do this in spite of equation (3.120) since experimental results indicate $\beta_{\mu\nu}$ correlates well with $S_{\mu\nu}$. Hence the off-diagonal Hamiltonian matrix elements are written as

$$H_{\mu\nu} = \beta_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} \quad \phi_\mu \text{ on A, } \phi_\nu \text{ on B} \tag{3.148}$$

where β^0_{AB} is a semiemperical parameter called the *bonding parameter*, chosen to depend only on the nature of the atoms A and B. This assumption is a reasonable one since bonding capacity increases with overlap. This is Mulliken's principle of maximum overlap. As mentioned above NDO is in direct conflict with this well known principle. CNDO then uses NDO with caution and compensates for the computational simplifications of NDO by the introduction of semiemperical relationships such as that illustrated by (3.148).

Using (3.145) in (3.137) gives the following equation for the diagonal Fock matrix element

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} P_{BB}\, \gamma_{AB} - V_{AB} \qquad \phi_\mu \text{ on atom A} \tag{3.149}$$

Equations (3.135) and (3.148) yield the following expression for the off-diagonal Fock matrix elements

$$F_{\mu\nu} = \beta^{0}_{AB}\, S_{\mu\nu} - \frac{1}{2} P_{\mu\nu}\gamma_{AB} \qquad \phi_\mu \text{ on atom A, } \phi_\nu \text{ on atom B} \tag{3.150}$$

When ϕ_μ and ϕ_ν are on the same atom A then $H_{\mu\nu} = 0$ from equation (3.144), and hence (3.135) becomes

$$F_{\mu\nu} = -\frac{1}{2} P_{\mu\nu}\, \gamma_{AA} \qquad \phi_\mu \neq \phi_\nu, \text{ both on atom A} \tag{3.151}$$

The net charge on any atom B is given by

$$Q_B = Z_B - P_{BB} \tag{3.152}$$

where Z_B is the core (nucleus plus inner shell electrons) charge of atom B and P_{BB} is the valence electronic density on atom B.

Using (3.152) in (3.149)

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} [-Q_B\gamma_{AB} + (Z_B\gamma_{AB} - V_{AB})] \qquad \phi_\mu \text{ on atom A} \tag{3.153}$$

The term $Z_B\gamma_{AB} - V_{AB}$ is called the *penetration integral*. $Z_B\gamma_{AB}$ represents the repulsion energy of any electron on A and any electron on B (via the two-electron repulsion integral) with the core of B. $-V_{AB}$ is the attractive interaction between any valence electron on atom A with the core of B. Hence the term "penetration integral".

Using equation (3.117) in equation (3.110)

$$E = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) \qquad (3.154)$$

This is the total electronic energy of the system. The nuclear-nuclear repulsion energy then may be added to give the expression for the total energy (ignoring nuclear kinetic energy) by using the Born-Oppenheimer approximation and replacing the nuclear charges with the core charges in equation (3.10). This gives

$$E = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{A<B} Z_A Z_B R_{AB}^{-1} \qquad (3.155)$$

This completes the basic derivation of the CNDO method. The main steps followed in this derivation are

(1) The Born-Oppenheimer approximation is used to separate nuclear and electronic motions, allowing the electronic Schroedinger equation to be written.

(2) A molecular orbital approach is taken. The molecular n-electron wavefunction is written, in the Orbital Approximation, as a product of n one-electron molecular orbitals, electron correlation being ignored.

(3) Molecular spin-orbitals are written as Slater determinants consistent with the Pauli Exclusion and Exchange Antisymmetry Principles.

(4) An expression for the electronic energy of the system is obtained in terms of a one-electron core-Hamiltonian and two-electron Coulomb and Exchange Integrals. The core-Hamiltonian is a three dimensional integral over the spatial coordinates of an electron, and represents the kinetic plus the potential energy of interaction of an electron with all the cores of the atoms in the molecular system (the term "core" implies the nucleus and inner electron-shells). The Coulomb integral is a six-dimensional integral over the spatial coordinates of any pair of electrons in the ith and jth

molecular orbitals and represents the repulsion energy between these two electrons in the region of overlap of the orbitals ψ_i and ψ_j. The Exchange Integral is also a six dimensional integral over the spatial coordinates of two electrons in the ith and jth molecular orbitals. It reflects the energy stabilization due to the partial correlation of electrons with parallel spins.

(5) The Variational Principle is now applied to the energy expression derived above to derive a set of differential equations for the optimum forms of the molecular orbitals. These are the Hartree-Fock equations which resemble the Schroedinger time-independent eigenequation with the Hamiltonian replaced by the Fock operator. The latter is an operator which incorporates the above-mentioned core-Hamiltonian, the Coulomb operator (analogous to the Coulomb integral) and the Exchange operator (analogous to the Exchange integral).

(6) The Roothaan equations are derived from the Hartree-Fock equations by expressing the molecular orbitals as Linear Combinations of Atomic Orbitals of the constituent atoms. For this purpose, all valence electrons of the atoms are treated explicitly and a valence basis set consisting of the atomic valence functions is used. The Roothaan equations differ from the Hartree-Fock equations in that they are algebraic rather than differential equations and also insofar as they involve the core Hamiltonian and the Coulomb and Exchange integrals in terms of atomic valence functions.

(7) The Neglect of Differential Overlap Approximation is now invoked and used in a semi-emperical manner. The overlap matrix is replaced by a unit matrix in the Roothaan equations and differential overlap is ignored in normalizing the molecular orbitals.

(8) Differential overlap is ignored in all two electron (Coulomb and Exchange) integrals in such a way that these are non-zero only if the overlap

of each electron's orbital is with itself. Otherwise the integral is taken to be zero. This is mathematically expressed as $(\mu\nu/\lambda\sigma)=(\mu\mu/\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}$. This automatically implies the neglect of all three- and four-centre terms.

(9) In order to restore rotational invariance, which is destroyed by the above step, an additional approximation is introduced. This makes all the two-electron (Coulomb and Exchange) integrals depend only on the nature of the atom to which the electron atomic orbital belongs and not on the nature of the orbital itself. This enables the introduction of a semi-emperical parameter, γ_{AB}, which depends solely on the pair A,B of atoms considered and expresses the average electrostatic repulsion between any electron on atom A and any electron on atom B. This means that all two integrals are written as $(\mu\nu/\lambda\sigma)=(\mu\mu/\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}=\gamma_{AB}$ for all ϕ_μ on any atom A, and all ϕ_ν on any other atom B. For all ϕ_μ on any atom A the (one-centre two-electron repulsion) integrals are written as $(\mu\nu/\lambda\sigma)=(\mu\mu/\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}=(\mu\mu/\mu\mu)=\gamma_{AA}$. γ is termed an *electron repulsion integral.*

(10) Differential overlap is ignored in the terms expressing the interaction energy of any valence electron on atom A with the core of any other atom B in the following manner. $<\mu|V_B|\mu> = V_{AB}$ for all ϕ_μ on A and $<\mu|V_B|\nu> = 0$ for all ϕ_μ,ϕ_ν on A. V_{AB} is the interaction energy of any valence orbital on atom A with the core (nucleus plus inner-shell electrons) of atom B and $-V_B$ is the potential energy field due to the nucleus and inner-shell electrons of atom B. This approximation results in expressions for the matrix elements core Hamiltonian given by $H_{\mu\mu}= U_{\mu\mu} - \sum_{B\neq A} V_{AB}$ for all ϕ_μ on A, and $H_{\mu\nu} = 0$ for all ϕ_μ,ϕ_ν on A with $\phi_\mu\neq\phi_\nu$. $U_{\mu\mu}$ is an atomic one-centre term which gives the energy of an electron in ϕ_μ in the field of the core of its own atom. $U_{\mu\mu}$ and V_{AB} are both obtained semi-emperically, giving the CNDO method added flexibility.

(11) The off-diagonal core-Hamiltonian matrix elements, $H_{\mu\nu}$, for the case where ϕ_μ and ϕ_ν are centred on different atoms A and B is taken to be proportional to the corresponding overlap integral, $S_{\mu\nu}$, with the constant of proportionality, β^0_{AB}, being another semi-emperical parameter. Hence, $H_{\mu\nu} = \beta^0_{AB} S_{\mu\nu}$, ϕ_μ on A, ϕ_ν on B. Hence, here differential overlap is not ignored. Experimental results indicate that there is good correlation between $H_{\mu\nu}$, which is called the resonance integral and denoted by $\beta_{\mu\nu}$, and the overlap integral $S_{\mu\nu}$.

(12) The CNDO equations are now solved in an iterative manner by the Self Consistent Field method. This method basically involves making an initial estimate of the molecular orbitals. Here previous experience is necessary to choose a set of molecular orbital coefficients which will give fast convergence. The coefficients of the approximate molecular orbitals are used to construct the density matrices $P_{\mu\nu}$ and the Fock matrix elements $F_{\mu\nu}$. The CNDO equations are then solved, for instance, by matrix diagonalization techniques. This yields a new set of coefficients for the molecular orbitals. The procedure is repeated until either the coefficients or the energy do not change by more than a predetermined amount. The wavefunctions thus obtained are said to be self consistent with the potential field (potential energy terms in the Fock matrix elements $F_{\mu\nu}$) they generate.

3.7.1 CNDO Parameterizations [19,86]

A complete CNDO calculation requires values for the overlap integrals $S_{\mu\nu}$, $U_{\mu\mu}$ and V_{AB} (i.e. the energy of an electron in the field of the core of its own atom and the interaction energy of any valence electron on A with the core of B, respectively) terms of the core Hamiltonian matrix, the electron repulsion integrals γ_{AB} and γ_{AA}, and finally, the bonding parameters β^0_{AB}. It is the manner in which these semi-emperical parameters are evaluated that gives rise to the different CNDO methods, CNDO/1, CNDO/2 and CNDO/S.

3.7.2 The CNDO/1 Parameterization

This is an earlier parameterization scheme of Pople and Segal [86]. CNDO/1 was later replaced by the much more successful scheme CNDO/2 [87], to be described below, and is seldom used nowadays. Nonetheless, a study of CNDO/1, especially in relation to CNDO/2, shows clearly the importance of choosing the "adjustable" parameters in a semi-emperical manner.

The CNDO/1 method can be used for atoms in the periodic table up to fluorine. The basis set ϕ_μ consists of Slater-type valence atomic orbitals. The overlap integrals are calculated by orthonormalizing $S_{\mu\nu}$

$$S_{\mu\nu} = \delta_{\mu\nu} \quad \text{for } \phi_\mu, \phi_\nu \text{ on the same atom A.}$$

Two centre overlap integrals are evaluated in a prolate spheroidal (also called confocal elliptical) coordinate system [19,97] in terms of a so-called reduced overlap integral [19] which is a function of the atomic orbital quantum numbers, n_a, l_a, m, n_b, l_b, α, β where n_a, n_b are the principal quantum numbers of the two orbitals (centred on atom A and B), l_a, l_b are the azimuthal quantum numbers, m is the magnetic quantum number, and α and β are the spin quantum numbers [19]. The scheme is described in detail by Pople and Beveridge in Appendix B of reference [19].

The two-electron repulsion integrals, γ_{AB}, are calculated in a similar manner using only the spherically symmetrical s orbitals, that is, no differentiation is made between s and p orbitals [19,88]. Hence

$$(\mu\mu/\lambda\lambda)=\iint\phi_\mu(1)\phi_\nu(1)\,\frac{1}{r_{12}}\,\phi_\lambda(2)\phi_\nu(2)\,d\tau_1 d\tau_2=\gamma_{AB}=\iint s_A^2(1)\,\frac{1}{r_{12}}\,s_B^2(2)\,d\tau_1 d\tau_2 \qquad \begin{array}{l}\phi_\mu\equiv s_A \text{ on A}\\ \phi_\nu\equiv s_B \text{ on B}\end{array} \tag{3.156}$$

and

$$(\mu\mu/\mu\mu)=\iint\phi_{\mu}^{2}(1)\,\frac{1}{r_{12}}\,\phi_{\mu}^{2}(2)d\tau_{1}d\tau_{2}=\gamma_{AA}=\iint s_{A}^{2}(1)\,\frac{1}{r_{12}}\,s_{A}^{2}(2)d\tau_{1}d\tau_{2}\quad \phi_{\mu}\equiv s_{A}\text{ on A} \tag{3.157}$$

Furthermore, the terms V_{AB} representing the interaction between a valence electron on A with the core (nucleus and inner-shell electrons) of other atoms B, are also calculated using s valence orbitals of A and treating the B core as a point charge at the position of the B nucleus. Hence

$$V_{AB} = Z_{B} \int s_{A}^{2}(1)(r_{1B})^{-1}d\tau_{1} \tag{3.158}$$

where Z_B is the core charge of B and r_{1B} is the distance of the valence electron from the B nucleus.

The terms $U_{\mu\mu}$, which are one-centre atomic terms expressing the total energy of an electron in orbital ϕ_μ in the field of the core of its own atom, could be calculated from atomic orbitals like the terms $S_{\mu\nu}$, γ_{AB} and V_{AB}. However, in CNDO/1 this is not done since better results are achieved when these parameters ($U_{\mu\mu}$) are obtained from experimentally observed atomic energy levels.

At the level of approximation used in the CNDO method, interaction energy between the valence electrons of an atom X (between Li and F in the periodic table) with an electronic configuration $(2s)^m$ $(2p)^n$ can be written as [19]

$$E(X,2s^{m},2p^{n}) = mU_{2s,2s} + nU_{2p,2p} + \frac{1}{2}(m+n)(m+n-1)\gamma_{AA} \tag{3.159}$$

since all two electron repulsion integrals would be γ_{AA} (from equation 3.129). An expression analogous to (3.159) may be written for the energy of the atomic cation X^+ formed by the removal of a 2p electron from X. Hence

$$E(X^{+},2s^{m},2p^{n-1})=mU_{2s,2s}+(n-1)U_{2p,2p}+\frac{1}{2}(m+n-1)(m+n-2)\gamma_{AA} \qquad (3.160)$$

The atomic potential of ionization from a 2s orbital is, by definition,

$$I_{s}(X,2s^{m},2p^{n})=E(X^{+},2s^{m-1},2p^{n})-E(X,2s^{m},2p^{n}) \qquad (3.161)$$

Now analogous to (3.157)

$$E(X^{+},2s^{m-1},2p^{n})=(m-1)U_{2s,2s}+nU_{2p,2p}+\frac{1}{2}(m+n-1)(m+n-2)\gamma_{XX} \qquad (3.162)$$

Using (3.162) and (3.155) with $\gamma_{AA}\equiv\gamma_{XX}$ in (3.161) yields

$$I_{s}(X,2s^{m},2p^{n})=-U_{2s,2s}-(m+n-1)\gamma_{XX} \qquad (3.163)$$

Similarly, the atomic potential of ionization from a 2p orbital is

$$I_{p}(X,2s^{m},2p^{n})=-U_{2p,2p}-(m+n-1)\gamma_{XX} \qquad (3.164)$$

Now since γ_{XX} are, in CNDO/1, calculated as described above, the terms $U_{\mu\mu}$ ($U_{2s,2s}$ and $U_{2p,2p}$) can be obtained from equations (3.163) and (3.164) by using experimental values for I_s and I_p. These values of ionization potential are given in Table 3.1 below.

Table 3.1 Ionization potentials (in ev) used to fix $U_{\mu\mu}$ in CNDO/1 [19]

Atom	H	Li	Be	B	C	N	O	F
I_{1s}	13.06							
I_{2s}		5.39	9.32	14.05	19.44	25.58	32.28	40.20
I_{2p}		3.54	5.96	8.30	10.67	13.19	15.85	18.66

The only unspecified parameter now is the bonding parameter β^{0}_{AB}. This is written as a sum of two equally contributing parts, each due to one atom.

$$\beta^0_{AB} = \frac{1}{2} (\beta^0_A + \beta^0_B) \qquad (3.165)$$

This reduces the amount of semi-emperical parameterization necessary. The values used in CNDO/1 are given below in Table 3.2

Table 3.2 Bonding parameters β^0_A (in ev) used in CNDO/1 [19]

Atom	H	Li	Be	B	C	N	O	F
$-\beta^0_A$	9	9	13	17	21	25	31	39

3.7.3 The CNDO/2 Parameterization [19,87]

This scheme differs from the one above in two respects. Firstly, it neglects penetration integrals (defined above) and secondly, it utilizes the emperical ionization potentials *and* electron affinities in order to fix the values for $U_{\mu\mu}$. The modifications are necessary to bring about closer agreement between computed and experimental results.

It is difficult to theoretically justify the neglect of penetration integrals. However, doing this, which is equivalent to assuming

$$Z_B \gamma_{AB} = V_{AB} \qquad (3.166)$$

does appear to compensate for errors of the opposite sign introduced by the neglect of differential overlap. Equation (3.164) can be rewritten as

$$-I_\mu = U_{\mu\mu} + (Z_A - 1) \gamma_{AA} \qquad (3.167)$$

where Z_A is the core charge and we have used the fact that in a neutral atom the total core charge, in atomic units, must equal the number of valence electrons (m+n in (3.164)). An analogous equation can be derived for atomic electron affinities, A_μ [19].

$$-A_\mu = U_{\mu\mu} + Z_A \gamma_{AA} \qquad (3.168)$$

From (3.167) and (3.168)

$$-\frac{1}{2}(I_{\mu} + A_{\mu}) = U_{\mu\mu} + (Z_A - \frac{1}{2})\,\gamma_{AA} \tag{3.169}$$

Using (3.166) (i.e. ignoring the penetration integral) and (3.152) in (3.153) yields

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2}\,P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A} P_{BB}\gamma_{AB} - Z_B\gamma_{AB} \tag{3.170}$$

from which, by using (3.169) the following equation is obtained.

$$F_{\mu\mu} = -\frac{1}{2}(I_{\mu}+A_{\mu}) + [(P_{AA}-Z_A) - \frac{1}{2}(P_{\mu\mu}-1)]\gamma_{AA} + \sum_{B\neq A} (P_{BB}\gamma_{AB}-Z_B\gamma_{AB}) \tag{3.171}$$

$$F_{\mu\mu} = -\frac{1}{2}(I_{\mu}+A_{\mu}) + [(P_{AA}-Z_A) - \frac{1}{2}(P_{\mu\mu}-1)]\,\gamma_{AA} + \sum_{B\neq A} (P_{BB}\gamma_{AB}-Z_B\gamma_{AB}) \quad \phi_{\mu} \text{ on atom A}$$

Using (3.165) in (3.150) and (3.151) yields

$$F_{\mu\nu} = \frac{1}{2}(\beta_A^0 + \beta_B^0)\,S_{\mu\nu} - \frac{1}{2}\,P_{\mu\nu}\,\gamma_{AB} \quad \phi_{\mu} \text{ on A, } \phi_{\nu} \text{ on B} \tag{3.172}$$

and

$$F_{\mu\nu} = -\frac{1}{2}\,P_{\mu\nu}\,\gamma_{AA} \quad \phi_{\mu}\neq\phi_{\nu}, \text{ both on A} \tag{3.173}$$

Equations (3.171), (3.172) and (3.173) are the basic equations of CNDO/2. Used with (3.142), (3.143), (3.144), (3.145), (3.148) and (3.155) the CNDO/2 energy for the molecular system bay be computed. The electronegativities, $-(I_{\mu} + A_{\mu})/2$, normally used in CNDO/2 are given below in Table 3.3 [19] together with the bonding parameters for elements of the first and second row of the periodic table.

CNDO/2 when applied to elements in the first row of the periodic table (up to F) is similar to CNDO/1 except for the two modifications concerning neglect of penetration integrals and use of atomic electronic affinities with ionization potentials. However, when applied to the elements in the second row of the periodic table (Na to Cl), an additional modification has been found to be necessary. In this case the bonding parameters are constrained by the following equation

$$\beta^\circ_{AB} = (K/2)(\beta^\circ_A + \beta^\circ_B)$$

where K = 0.75 for second-row and unity for first-row elements. Furthermore, the bonding parameter for a second row element A, β°_A, is assumed to be related to the atomic one-centre core terms $U_{\mu\mu}$ of an atom C in the first row by [19]

$$\beta^\circ_A = \beta^\circ_C \frac{U_{3s,3s}(A) + U_{3p,3p}(A)}{U_{2s,2s}(C) + U_{2p,2p}(C)}$$

where the $U_{\mu\mu}$ terms are governed by equation (3.167). The values of β for the second row shown in Table 3.3 are calculated in this manner.

3.8 The CNDO Method in Spectroscopy, CNDO/S [20-34]

The methods described above, CNDO/2, in particular have been quite successful in describing the ground electronic states of moderately large (containing up to about 35 atoms or 80 basis functions, whichever is smaller) molecules [19]. As described in the above sections, CNDO/1 and CNDO/2 are methods of the Hartree-Fock level of computation which give approximate values of the lowest (ground) electronic states.

For a description of the excited states and spectra of a molecule or a molecular complex it is necessary to extend this method. Although various attempts have been made at this [98-103] none of them have been as successful as the CNDO/S method introduced by J. Del Bene and H.H. Jaffé in 1968 [20]. This method involves using the basic SCF CNDO/2 wavefunctions with a limited amount of *configuration interaction* utilizing only singly excited (relative to the CNDO/2 wavefunctions) orbitals. The CNDO/S method requires certain changes in parameterization, in the way that two-electron repulsion integrals are calculated and in the treatment of the σ and π electrons. Hence for instance, whereas CNDO/2 is parameterized for agreement with *ab initio* ground state wavefunctions of diatomic molecules using Slater determinants as trial functions, CNDO/S is parameterized on spectroscopic transitions using Virtual Orbital-Configuration Interaction (VO-CI) trial functions. This is an important point to keep in mind since the parameterization of a semi-emperical method is valid only with the set of trial functions for which it has been calibrated. If different trial functions are used, a complete reparametrization, or at least verification that the calibration is valid within the particular approximation used, is required [18]. Before

Table 3.3 Electronegativities and Bonding Parameters (in ev)used in CNDO/2 [19]

Atom	H	Li	Be	B	C	N	O	F
$(I_s+A_s)/2$	7.176	3.106	5.946	9.594	14.051	19.316	25.390	32.272
$(I_p+A_p)/2$		1.258	2.563	4.001	5.572	7.275	9.111	11.080
$(I_d+A_d)/2$								
$-\beta_A^0$	9	9	.13	17	21	25	31	39
$(I_s+A_s)/2$	Na	Mg	Al	Si	P	S	Cl	
$(I_p+A_p)/2$	2.804	5.125	7.771	10.033	14.033	17.650	21.591	
$(I_d+A_d)/2$	1.302	2.052	2.995	4.133	5.464	6.989	8.708	
$-\beta_A^0$	0.150	0.162	0.224	0.337	0.500	0.713	0.977	
	7.7	9.4	11.3	13.1	15.1	18.2	22.3	

the details of CNDO/S are described, the method of configuration interaction, which it uses, will be outlined.

3.8.1 The Method of Configuration Interaction [104]

The Configuration Interaction (CI) technique can, in principle, be applied to any state of an atomic or molecular system. In this method the wavefunction is written as a linear combination of a set of Slater determinants, built, in turn, from a set of orthonormal, linearly independent, basis atomic functions [97]. Hence the molecular wavefunction is written as

$$\Psi(1,2, \ldots . n) = \sum_j C_j D_j(1,2, \ldots . n) \tag{3.174}$$

where $D_j(1,2, \ldots . n)$ is a Slater determinant of the type described by any of the equations (3.31) to (3.35), or a linear combination of such determinants. Each of the terms D_j hence is made up of n one-electron molecular orbitals orthornormalized according to equation (3.38). Each of the molecular orbitals is in turn normally written as an LCAO function as given by equation (3.85) [105]. The functions D_j are called configurations or configuration functions. They are chosen by experience and by some trial and error depending on the electronic state of the system under consideration. Hence, for example, if a singlet state is being considered the configurations used would be singlet wavefunctions. Similarly for doublet and triplet states.

Configuration Interaction methods can be applied to ground-state wavefunctions as well as excited state wavefunctions. Generally, however CI is much more important for the description of excited states than for ground states.

If CI is considered for a ground singlet state of a molecular system then a reasonable choice of the leading term, $C_0D_0(1,2, \ldots . n)$, in the CI expansion (3.174) would be the Self Consistent Field Wavefunction obtained, for example, from a CNDO/2 treatment. The other configurations would be singlet wavefunctions excited to various degrees (singly, doubly etc.) Hence

$$C_0D_0 = \Pi\ \Psi(1,2,\ldots.n) = \Pi\left|\psi_1(1)\bar{\psi}_1(2)\ldots.\psi_\mu(1)\bar{\psi}_\mu(1)\ldots\bar{\psi}_n(n)\right| \quad (3.175)$$

The other terms in the expansion (3.174) are formed by promoting one or more electrons from an occupied to an unoccupied ("virtual") SCF ground state wavefunction. The number of electrons promoted defines the degree of excitation of the CI expansion function. Hence a wavefunction which differs from the ground electronic wavefunction (3.175) by the promotion of one electron to a virtual orbital is "singly excited". Two promoted electrons yield a "doubly excited" configuration, etc. An example of a singly excited configuration would be

$${}^{\mu\nu'}D_0 = \left|\psi_1(1)\bar{\psi}_1(2)\ \ldots\ \psi_\mu(1)\bar{\psi}_{\lambda'}(i+1)\ \ldots\ \bar{\psi}_n(n)\right| \quad (3.176)$$

where the (i+1)th electron has been promoted from an occupied molecular orbital ψ_μ to an orbital (unoccupied in the SCF ground wavefunction) $\psi_{\lambda'}$. The superscripts $\mu\nu'$ on D_0 describe this. The second term in (3.174) could then be written as

$$C_1D_1 = C_1\{\left|\psi_1(1)\bar{\psi}_1(2)\ldots\psi_\mu(1)\bar{\psi}_{\lambda'}(i+1)\ldots\bar{\psi}(2n)\right| - \left|\psi_1(1)\bar{\psi}_1(2)\ldots \psi_{\lambda'}(1)\bar{\psi}_\mu(i+1)\ldots\bar{\psi}_n(2n)\right|\} \quad (3.177)$$

Some examples of doubly excited configurations are

$${}^{\mu\mu\lambda'\lambda'}D_0 = \left|\psi_1(1)\bar{\psi}_1(2)\ \ldots\ \psi_{\lambda'}(1)\bar{\psi}_{\lambda'}(i+1)\ \ldots\ \bar{\psi}_n(n)\right| \quad (3.178)$$

$${}^{\mu\mu\lambda'\kappa'}D_0 = \{\left|\psi_1(1)\bar{\psi}_1(2)\ldots\psi_{\lambda'}(1)\bar{\psi}_{\kappa'}(i+1)\ldots\bar{\psi}_\mu(n)\right| - \left|\psi_1(1)\bar{\psi}_1(2)\ \ldots \psi_{\kappa'}(1)\psi_{\lambda'}(i+1)\ldots\bar{\psi}_n(n)\right|\} \quad (3.179)$$

etc.

The wavefunctions chosen are eigenfunctions of the spin operators $\overline{S}^2$ and s_z. Hence singlet wavefunctions are eigenfunctions of $\overline{S}^2$ with eigenvalue zero. Doublet and triplet wavefunctions are eigenfunctions of $\overline{S}^2$ with eigenvalues of 3/4 and 2 respectively [18].

Examples of singly excited triplet configuration functions are given below [18]

$$^{\mu\lambda'}T^{1} = |\psi_1(1)\overline{\psi}_1(2) \ldots \psi_\mu(1)\psi_\lambda,(1+1) \ldots \psi_n(n)| \qquad (3.180)$$

$$^{\mu\lambda'}T^{0} = \{|\psi_1(1)\overline{\psi}_1(2)\ldots\psi_\mu(1)\overline{\psi}_\lambda,(1+1)\ldots\psi_n(n)|+|\psi_1(1)\overline{\psi}_1(2)\ldots\psi_\lambda,(1)\overline{\psi}_\mu(1+1)\ldots \overline{\psi}_n(n)|\} \qquad (3.181)$$

$$^{\mu\lambda'}T^{-1} = |\psi_1(1)\overline{\psi}_1(2) \ldots \overline{\psi}_\mu(1)\overline{\psi}_\lambda,(1+1) \ldots \overline{\psi}_n(n)| \qquad (3.182)$$

These three components of the triplet are distinguished by eigenvalues of $\overline{s}_z$, 1, 0 and -1, respectively, which are used as right superscripts.

Similar wavefunctions can be defined for doublets, quartets etc.

It turns out that the most important configurations are the singly and doubly excited functions. CNDO/S, uses only singly excited configurations.

The simplest way to describe an excited state is by the *Virtual Orbital* Approximation [18]. In this the excited state is described by a single configuration of the types given by equations (3.176) to (3.182) depending on the multiplicity (singlet, doublet, triplet etc.) of the state, with the provision that the ψ entering into these configurations are the molecular orbitals obtained in the solution for the ground state. This type of description is useful because of its simplicity and several important concepts such as those of $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions, are based on this approximation. Unfortunately, such a description of excited states is frequently not sufficient because although in many cases the first excited state of a molecule can be reasonably well defined by a single configuration, higher excited states cannot [18].

The Virtual Orbital Approximation can be improved by introducing Configuration Interaction. In this (VO-CI) method, the excited state functions are written as a sum (see equation (3.174)) of singly and doubly (and possibly even higher order) configuration functions such as those given by equations (3.175) to (3.182). Hence whereas the VO approximation uses only a single configuration for describing an excited state, the VO-CI method uses a series of these terms.

The configurations D_j are chosen so that they satisfy all, or if that is not possible, at least some of the symmetry conditions which the total wavefunction Ψ is required to satisfy. The fact that Slater determinants are used implies that the primary requirement, permutational antisymmetry, is satisfied. The linear combination of Slater Orbitals which make up D_j are, as mentioned above, spin adapted (eigenfunctions of the operators $\bar{S}^2$ and $\bar{s}_z$). Furthermore, they are also symmetry adapted satisfying the space symmetry requirements of the species (irreducible representation) of the molecular point group. Making each term in the CI expansion conform to spin and space symmetry conditions enforces these same conditions on the total wavefunction thereby providing a classification for the excited state being computed.

Further simplification which results from such a use of group theory is illustrated by substituting the CI expansion (3.174) into the Schroedinger time-independent waveequation (3.1) to yield

$$\sum_j (HD_j - ED_j)C_j = 0 \qquad (3.183)$$

Premultiplying by $C_i{}^*D_i{}^*$ and integrating over all space gives

$$(H_{ij} - ES_{ij})C_jC_i^* = 0 \tag{3.184}$$

where

$$H_{ij} = \langle D_i|\mathcal{H}|D_j\rangle \tag{3.185}$$

$$S_{ij} = \langle D_i|D_j\rangle \tag{3.186}$$

For (3.184) to have a non-trivial solution, the following secular equation must be satisfied

$$|H - SE| = 0 \tag{3.187}$$

with the matrix elements H_{ij} and S_{ij} as defined above. Since the matrix elements H_{ij} vanish if D_j and D_i belong to different symmetry species, use of group theory then simplifies the matter considerably, dividing the problem of computing the electronic state of a molecule into separate, smaller problems, one for each symmetry species.

The coefficients C_j of the CI expansion (3.174) are obtained essentially from the solution of equation (3.187). This is usually done by a tridiagonalization technique (in which all elements in the matrix except those on the main diagonal and on the two immediately adjacent diagonals, one on each side, are zero) devised by Householder [106]. The Householder method is one of the more efficient methods of solving eigenequations (for eigenvalues and eigenvectors) and is the principal method in use today in many computer programs. The published form of CNDO/S [35] uses this method.

To recapitulate, the CI method, including the VO-CI CNDO/S technique, involves the following four main procedures [104].

(1) Choosing a basis set $\{\phi_\mu\}$ (see equation (3.85)). In most treatments an atomic basis set of the type used in the SCF Hartree-Fock approach with

perhaps some additional functions to incorporate the effect of electron correlation is adequate. Hence, for instance, the CNDO/2 basis functions also form the basis set in CNDO/S. The Coulomb and Exchange Integrals and the Hamiltonian matrix elements as given by equations (3.102), (3.104) and (3.93) are evaluated, as in the general CNDO method in terms of these atomic basis functions.

(2) Forming LCAO-MO's (equation (3.85). Here it is normal practice to use the SCF occupied and virtual orbitals because these orbitals which maintain the SCF boundary between the occupied and virtual subspacesare about as effective, in general, as any other reasonable choice of molecular orbitals [104]. These orbitals are then used to transform the above mentioned integrals to the forms using molecular orbital basis sets (equations of the type given by (3.58), (3.59) and (3.53)).

The above two steps are similar to those described for the general CNDO method and to the CNDO/1 and CNDO/2 techniques.

(3) Choosing and constructing a set of symmetry adapted configuration functions appropriate to the state or states. The VO-CI approximation is used and configurations excited to various degrees are used in the CI expansion as described above. The Hamiltonian matrix is then calculated in terms of these configuration functions.

(4) The Schroedinger eigenequation is then solved by standard diagonization techniques such as that of Householder.

3.8.2 CNDO/S Parameterization [18,20]

CNDO/S is a VO-CI method of the type described above. Having been developed with the specific purpose of describing the excited electronic states and spectra of molecules, it uses a different set of CNDO parameters in order to achieve this goal.

The CNDO/1 and CNDO/2 parameterizations approximate all two-electron repulsion integrals between different orbitals as between a pair of 2s orbitals and calculate this quantity from Slater type atomic orbitals. In CNDO/S Del Bene and Jaffé [20] retained many of the proven features of the Pariser-Parr-Pople (PPP) method for pi electrons [107-109]. Accordingly, one-centre electron repulsion integrals γ_{AA} (see equations (3.129) and (3.130)) are set equal to

$$\gamma_{AA} \equiv \gamma_{\mu\mu} = I_{\mu}^{A} - A_{\mu}^{A} \text{ for } \phi_{\mu} \text{ on atom A} \tag{3.188}$$

where I_{μ}^{A} and A_{μ}^{A} are the ionization potential and electron affinity of the ϕ_{μ} orbital of atom A.

Two-centre electron repulsion integrals are approximated in two different ways. It has been found that for singlet states the approximation due to Mataga [57] works best. In this case the integral $\gamma_{\mu\nu}$ is written as follows

$$\gamma_{\mu\nu} = \gamma_{AB} = (\mu\mu/\nu\nu) = [r_{AB} + 2/(\gamma_{\mu\mu} + \gamma_{\nu\nu})]^{-1} \tag{3.189}$$

In treating tripletstates the approximation due to Pariser is used. In this case the two-centre electron repulsion integrals are estimated by the charged-sphere method [88, 108, 110] in which p orbitals are replaced by two charged spheres touching the corresponding nucleus. The repulsion between two sets of such charged spherical clouds is taken as an approximation to the two-centre electron repulsion energy and is given by

$$\gamma_{AB} = (1/2r_{AB}) (1 + \rho) \tag{3.190}$$

with

$$\rho = [1 + (4R^2/r_{AB}^2)]^{-1/2} \tag{3.191}$$

where

R is the radius of the charged spheres

r_{AB} is the internuclear distance between atoms A and B

R is chosen so that γ_{AB} is equal to the integral $(p_\pi^A p_\pi^A | p_\pi^B p_\pi^B)$ at preset distances r_{AB}.

The second change involved in CNDO/S is in its treatment of the bonding parameters β. In CNDO/1 and CNDO/2 this parameter is defined, by equations (3.148) and (3.165) as

$$\beta_{\mu\nu} = \frac{1}{2} S_{\mu\nu} (\beta_A^0 + \beta_B^0) \qquad (3.192)$$

with β_A^0 and β_B^0 being adjustable parameters which have been chosen so as to best reproduce *ab initio* calculations on diatomic molecules. In CNDO/S the calculation of the overlap integral S in equation (3.192) is modified by decomposing it into two parts, a σ and a π component. The σ component is calculated in the normal way (as in CNDO/1 and CNDO/2) from Slater s orbitals. The π component is also calculated in this manner but is multiplied by a factor *k* the optimum value of which Del Bene and Jaffé give as 0.585. The bonding parameters in CNDO/S hence are given by

$$\beta_{\mu\nu} = \frac{1}{2} (S^\sigma_{\mu\nu} + kS^\pi_{\mu\nu})(\beta_A^0 + \beta_B^0) \qquad (3.193)$$

Finally, the third change made is the recalibration of β_A^0. These values of β are shown below in Table 3.4 [35] and should be compared with the values used in CNDO/1 and CNDO/2 and given in Tables 3.2 and 3.3.

Table 3.4 Bonding Parameters (in ev) used in CNDO/S [35]

Atom A	H	Li	Be	B	C	N	O	F
$-\beta_A^0$(ev)	12.0	9	13	5	17.5	26.0	45.0	50.0

The CNDO/S method has been particularly useful in describing the electronic states of several molecules [20-34].

In the present work, the application of CNDO/S is extended to Contact Charge Transfer complexes [36,37]. In particular, the following chapter deals with CNDO/S calculation of the excited states of contact CT complexes of several donors with the O_2 molecule.

CHAPTER IV

CNDO/S COMPUTATIONS

This chapter describes results obtained by the application of the CNDO/S method to complexes of benzene (C_6H_6), aniline ($C_6H_5NH_2$), pyrrole (C_4H_4NH) and H_2O with O_2. The results obtained are discussed and compared with experimental data available to date. Before such a comparison can be made, however, it is necessary to briefly describe the orbital wavefunctions of the molecules involved. This is done in section 4.1. Experimental work of other researchers, which is correlated to the computations performed here, is outlined in section 4.2. Section 4.3 briefly discusses the computer coding of CNDO/S together with the options available. (The complete program is listed in Appendix 1). Section 4.4 details the types of calculations made and the configurations of the complexes investigated. (A sample calculation is given in full in Appendix 2). Results are presented in section 4.5 and discussed in relation to the experimental work outlined in section 4.2. It is shown that CNDO/S computations accurately describe the behaviour of contact CT complexes, reproducing experimental data and predicting values for such quantities as contact radii and energies of formation which have not been measured yet. Section 4.6 concludes this chapter.

4.1 Molecular Orbitals Description of the Monomers

A description of the molecular orbital wavefunctions is essential in understanding and interpreting the results obtained. An understanding of the shapes of these wavefunctions explains why, for example, certain atoms in a given donor act as the major electron density contributors in the formation of a particular charge-transfer state. It also enables us to tell which m.o.s are involved in a given CT transition.

4.1.1 Molecular Orbitals of Benzene, Aniline and Pyrrole

The molecular orbitals of importance to us are the least bound ones which are formed by the valence electrons of the constituent atoms. Hence the π and n molecular orbitals are the ones that account for the donor properties of these molecules. The σ frameworks are, to that extent, relatively unimportant.

The benzene molecule is the easiest of the three organic donors to treat. Its high symmetry (C_{6v}) enables group-theoretical principles to be applied in a relatively simple treatment.

In benzene the π molecular orbital wavefunctions can be fairly accurately described by using Linear Combination of the carbon 2p Atomic Orbitals, one from each carbon atom. Using group-theoretical principles these π m.o.s can be written as follows [61].

$$\psi(A) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \tag{4.1}$$

$$\psi(E_1a) = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) \tag{4.2}$$

$$\psi(E_1b) = \frac{1}{2} (\phi_2 + \phi_3 - \phi_5 - \phi_6) \tag{4.3}$$

$$\psi(E_2a) = \frac{1}{\sqrt{12}} (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \tag{4.4}$$

$$\psi(E_2b) = \frac{1}{2} (\phi_2 - \phi_3 + \phi_5 - \phi_6) \tag{4.5}$$

$$\psi(B) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \tag{4.6}$$

Here ϕ_i represents a 2p orbital of the ith carbon atom in the benzene ring.

$\psi(A)$ is the most strongly bonding molecular orbital of the six described above. $\psi(E_1a)$ and $\psi(E_1b)$ are degenerate in the Huckel Approximation [61] and are somewhat less bonding in character than $\Psi(A)$. $\psi(E_2a)$ and $\psi(E_2b)$ are, once again in the Huckel Approximation, degenerate, and antibonding in character, while $\psi(B)$ is the most antibonding of all.

The bonding and antibonding characters can be understood qualitatively in terms of the nodal planes in these wavefunctions. Hence $\psi(A)$ has no nodal planes. $\psi(E_1a)$ and $\psi(E_1b)$ both have one nodal plane - hence the subscript 1. The nodal plane in $\psi(E_1b)$ passes through diametrically opposite carbon atoms (say C1 and C4). The nodal plane in $\psi(E_1a)$ is perpendicular to the nodal plane in $\psi(E_1b)$. $\psi(E_2a)$ and $\psi(E_2b)$ each have two nodal planes as indicated by the subscript 2. The nodal planes in $\psi(E_2b)$ are perpendicular to each other, one of them passing through diametrically opposite carbon atoms. The nodal planes in $\psi(E_2a)$, on the other hand result in the largest concentration concentration of electronic charge on the two atoms through which one of the nodal planes of $\psi(E_1b)$ passes.

The molecular orbitals of aniline and pyrrole are somewhat more difficult to treat. It is thought [130] that in aniline the nitrogen atom uses sp^2 hybridization [133] in the formation of three single bonds with the two hydrogen atoms and the carbon atom of the benzene ring. The HNH angle is therefore 120°, and the non-bonding orbital is thought to be an almost pure nitrogen atom 2p orbital.

There is some controversy [130,131,132] regarding the molecular electronic structure of pyrrole (and other similar five-membered heterocyclic compounds such as furan and thiophene). Pyrrole may be regarded essentially as a cyclic diene (that is a compound having two carbon-carbon double bonds). It is a conjugated diene because the two carbon-carbon double bonds alternate with single bonds. The lone pair of electrons of the N atom in pyrrole is thought to play a significant role in the formation of the planar aromatic ring of this molecule which is similar to the six π electron ring of benzene. (Each of the four carbon atoms contributes one 2p electron while the nitrogen atom contributes its "lone pair" to give a six electron π molecular orbital [132]).

4.1.2 Molecular Orbitals of H_2O

The molecular orbitals of H_2O have been studied quite extensively by several workers [134-140]. The oxygen atom has the electronic configuration $1s^2$, $2s^2$, $2p_x^2$, $2p_y$, $2p_z$. The OH bonds are fairly accurately described as being due to the overlap of a nearly pure 2p orbital of O with the 1s orbital of H. There are two lone pairs of electrons in the H_2O molecule residing in non-bonding orbitals. The latter are due to sp hybridization in the O atom [134]. These two non-bonding orbitals form two lobes, symmetrically located above and below the molecular plane subtending, roughly, tetrahedal angles with the OH bonds. The HOH angle is 104.5°.

4.1.3 Molecular Orbitals of O_2 [52]

As mentioned previously, the electronic configuration of atomic oxygen is $1s^2$, $2s^2$, $2p_x^2$, $2p_y$, $2p_z$. There are relatively large separations between the 1s and 2s orbitals, between the 2s and 2p orbitals, and again between the 2p and still higher orbitals. This implies that the parentage of the molecular orbitals in O_2 is fairly simply related to these isolated atomic orbitals.

For our purposes the following approximate description of the molecular orbitals of O_2 provides an adequate model for understanding the acceptor role of O_2.

The tightly bound 1s orbitals, one on each oxygen atom, give rise to two σ molecular orbitals one of which is bonding and the other antibonding.

These m.o.'s may be designated the symbols $\sigma(1s)$ and $\sigma^*(1s)$ respectively. Similarly, the two 2s atomic orbitals give rise to a $\sigma(2s)$ m.o. and a $\sigma^*(2s)$ m.o.. Hence, if one of the oxygen atoms is denoted by A and the other by B then the in-phase m.o. combinations of the s orbitals can be expressed as

$$\sigma(1s) \propto \phi_A(1s) + \phi_B(1s) \tag{4.7}$$

$$\sigma(2s) \propto \phi_A(2s) + \phi_B(2s) \tag{4.8}$$

and the out-of-phase m.o. combinations are governed by the relations

$$\sigma^*(1s) \propto \phi_A(1s) - \phi_B(1s) \tag{4.9}$$

$$\sigma^*(2s) \propto \phi_A(2s) - \phi_B(2s) \tag{4.10}$$

Here σ and σ^* are O_2 bonding and antibonding m.o.'s and ϕ_A, ϕ_B denote the atomic wavefunctions.

If the z axis is taken to be coincident with the O_2 molecular axis then the atomic $2p_z$ orbitals also give rise to bonding and antibonding σ m.o.'s. Hence

$$\sigma(2p_z) \propto \phi_A(2p_z) + \phi_B(2p_z) \tag{4.11}$$

and

$$\sigma^*(2p_z) \propto \phi_A(2p_z) - \phi_B(2p_z) \tag{4.12}$$

The atomic $2p_x$ and $2p_y$ orbitals give rise to π bonding and antibonding orbitals

$$\pi(2p_x) \alpha \phi_A(2p_x) + \phi_B(2p_x) \qquad (4.13)$$

$$\pi^*(2p_x) \alpha \phi_A(2p_x) - \phi_B(2p_x) \qquad (4.14)$$

$$\pi(2p_y) \alpha \phi_A(2p_y) + \phi_B(2p_y) \qquad (4.15)$$

$$\pi^*(2p_y) \alpha \phi_A(2p_y) - \phi_B(2p_y) \qquad (4.16)$$

These m.o.'s lie in the following order, from the most to the least tightly bound: $\sigma(1s)$, $\sigma^*(1s)$, $\sigma(2s)$, $\sigma^*(2s)$, $\sigma(2p_z)$, $\pi(2p_x)$ and $\pi(2p_y)$, $\pi^*(2p_x)$ and $\pi^*(2p_y)$, and $\sigma^*(2p_z)$. $\pi(2p_x)$ has the same energy as $\pi(2p_y)$ while $\pi^*(2p_x)$ and $\pi^*(2p_y)$ are also degenerate. The total number of electrons available from the two atoms is 16. These occupy the m.o.'s in accordance with Pauli's Exclusion Principle. Hence four electrons reside in the $\sigma(1s)$ and $\sigma^*(1s)$ orbitals and make no net contribution to the bonding in O_2. Similarly four more electrons reside in the $\sigma(2s)$ and $\sigma^*(2s)$ orbitals. Once again, as both bonding and antibonding orbitals are filled, there is no net binding. Of the remaining 8 electrons, 6 occupy the three bonding orbitals $\sigma(2p_z)$, $\pi(2p_x)$ and $\pi(2p_y)$. These contribute a bond order of three. The remaining two electrons may give rise to either a singlet or triplet state of O_2 depending on whether or not they occupy the same or different antibonding m.o. [52,141]. Hence if the remaining two electrons singly occupy the $\pi^*(2p_x)$ and $\pi^*(2p_y)$ m.o.'s with parallel spins then a triplet state ${}^3\Sigma_g^-$ results. This is the least energetic of the possibilities, and hence, the ground state of O_2 is $^3\Sigma_g^-$. If the electrons are paired and occupy one of the two π^* antibonding orbitals then the resulting state is a singlet, the $^1\Delta_g$ state, which lies 0.97ev above the $^3\Sigma_g^-$ ground state.

4.2 Experimental Evidence for Contact CT Complexes

The first experimental evidence for the existence of complexes of some organic molecules (including benzene, aniline and pyrrole) with oxygen was obtained by Evans [121-125] in the fifties. This was followed by the more extensive work of Tsubomura and Mulliken [49] which was conducted in 1960. The absorption spectrum of the complex of H_2O with O_2 was investigated by Heidt and his co-workers [116-117] in the late fifties. Somewhat more recently (1973) Birks *et.al.* [126] have investigated the benzene-oxygen complex in the vapor phase. The experimental work of Evans, Tsubomura and Mulliken, and Birks provides the basis for judging the results obtained by CNDO/S computations and shown in Figures 4.1 to 4.4 and Tables 4.1 to 4.4.

Birks *et.al.* measured the absorption spectrum of the benzene-oxygen contact CT complex from 2350 to 2120 Å from the difference in the absorption spectra of benzene vapor (70 torr) in the presence and absence of oxygen (760 torr). They found that the complex has an absorption maximum at 5.65ev (2190 Å) and has an energy of formation of 2.90ev from the benzene cation and oxygen anion.

The experimental work of Evans, Tsubomura and Mulliken, and Heidt *et.al.* was performed in the liquid phase. Tsubomura and Mulliken established that the absorption spectra they measured were due to contact CT complexes since they found that these spectra disappeared completely when nitrogen gas was bubbled through the liquid solution of the oxygen in the organic substance. This indicated that the observed spectra were not due to any stable ground state complex but to weak interactions between the organic donor and the oxygen acceptor molecules.

4.3 Computer Coding of CNDO/S

The computer program used in this work was QCPE No. 174 [35], obtained from Quantum Chemistry Program Exchange, Indiana University. Some modifications were necessary before it could be executed on the University's Amdahl computer. The program was developed by J. Del Bene, H.H. Jaffé, R.L. Ellis and G. Kuehnlenz.

QCPE 174 (see Appendix 1) is written in two parts. The first part is a preprocessor written in PL/I. The main program is written in fortran. The fortran preprocessor provides for variable dimensions in a fortran program. It scans for the presence of an alphanumeric variable name where a dimension specification would be expected and replaces the variable name with the correct numeric value. The latter has to be supplied by the user and will depend on the number of atoms in the system and the number of basis functions.

The main program has been written in such a way that a given molecular system can be examined under numerous options. An input list governs the type of calculation that will be performed. In the default option, obtained if the option cards in the input list are left blank, the program executes CNDO/S calculations using the Mataga Approximation and configuration interaction for singlet states only. The options included are the following:

1. The maximum number of iterations permitted in obtaining convergence within specified limits in the SCF procedure.
2. The number of configurations to be included in CI
3. The type of electron repulsion integrals used. These can be evaluated by either the Mataga Approximation [18,57,111,112], the Pariser Approximation

[108], the Ohno Approximation [113,114] or the Roothaan theoretical method.

4. No CI and no excitation energies, CI for singlets only, CI for triplets only or CI for singlets and triplets.

5. The type of nuclear (core) repulsion integral used. This could be either the approximation that assumes these core to be point charges, the gammas described in Chapter III, or the Dewar formula [88,115].

6. The types of bonding parameters, β_0. These could be either the CNDO/S values of Del Bene and Jaffé, the CNDO/2 values of Pople *et.al.*, or those of Mulliken.

7. The charge densities of the excited states. These can be calculated together with the differences relative to the ground state for singlets alone, triplets alone, or for both the singlets and triplets.

8. SCF convergence tests. This could be done either on the total energy, the energies of occupied orbitals or on the electron density matrix.

9. Spectroscopic transitions. Here transitions between S_J and S_0, S_J and S_1, T_J and S_0, and T_J and T_1 can be calculated.

QCPE 174 is listed in Appendix 1.

4.4 Method

CNDO/S calculations were carried out for the complexes of benzene, aniline, pyrrole and H_2O with molecular oxygen. These are some of the contact CT complexes for which experimental results in absorption have been obtained [16,49,116,117]. Computations were carried out using 60 singly excited configurations (relative to a closed-shell SCF reference wavefunction) for each complex. Two centre electron repulsion integrals were calculated using the Mataga Approximation for singlet energy values and by the Pariser Approximation for triplet states. A computation was abandoned if SCF energy convergence to within 0.0000lev was not obtained in 40 iterations.

Computations were carried out for one-to-one associations. The CNDO parameters used are given in Table 1 of reference [36].These values have been used in successfully explaining the electronic spectra of many molecules previously [20-34].

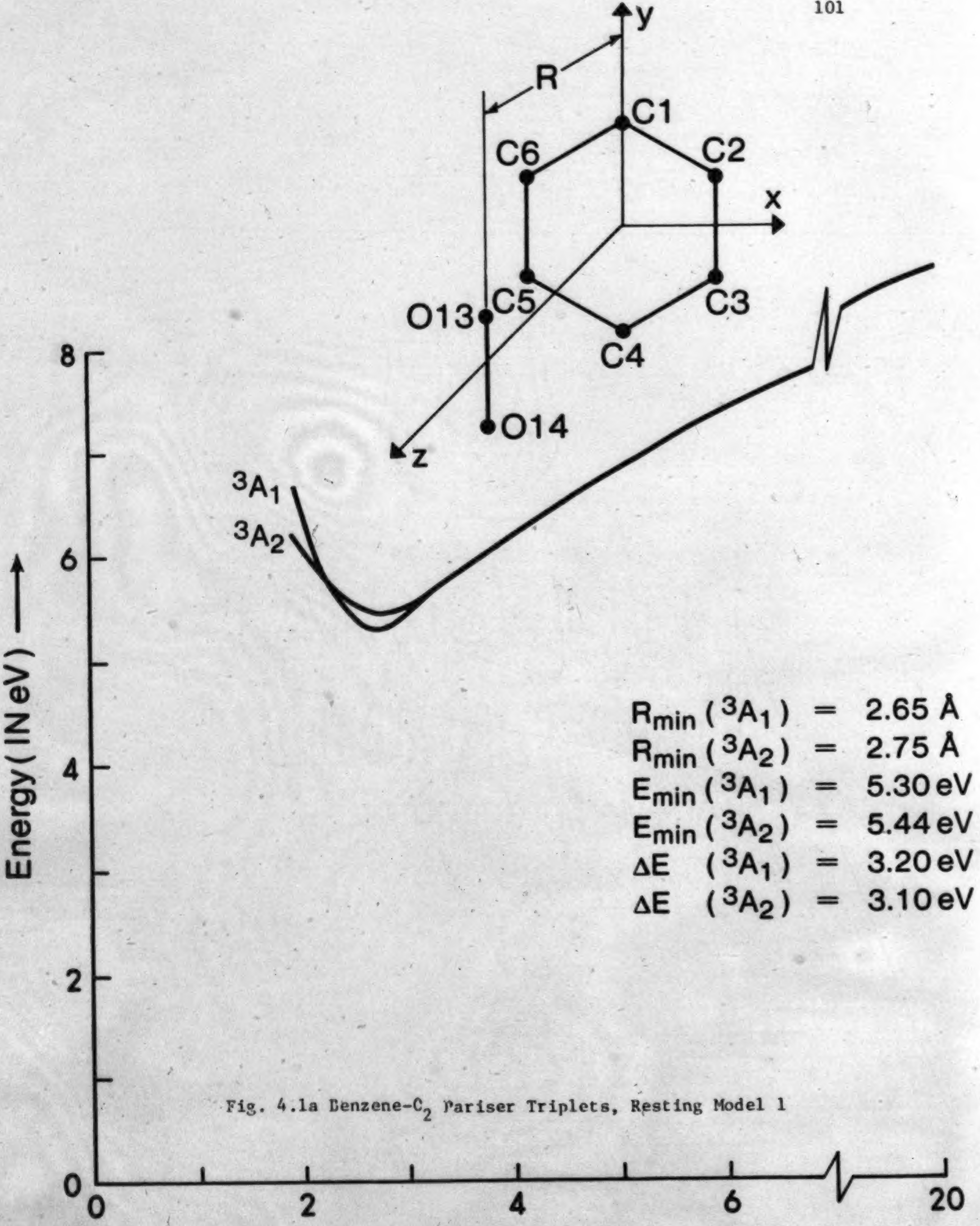
For each of the three organic molecules, CNDO/S calculations were carried out for three mutually orthogonal geometries. These configurations are referred to as the axial modal, resting model 1 and resting model 2 depending on the orientation of the linear O_2 molecule relative to the planar ring of the aromatic molecule. (See Figures 4.1, 4.2 and 4.3). For the H_2O-O_2 collision computations were performed for six planar configurations called models M1 to M6 (See Figure 4.5).

Singlet and triplet energy values were calculated for increments in R, the collisional parameter (See Figures 4.1, 4.2, 4.3, 4.4 and 4.5) of 1 Å for the most part, except near the potential energy triplet minima where smaller variations (between 0.05 Å and 0.1 Å) were used, in order to define these minima more accurately.

The atomic coordinates used in every instance were equilibrium ground electronic state values calculated by using the bond lengths and angles given by L.E. Sutton [118]. Except for the distance R, between the donor and acceptor molecules, all coordinates were held fixed at these values. The electron density on every atom together with the difference between the density in an excited state and that in the ground state was also calculated for every state treated at every value of R. A sample computer output is given in Appendix 2.

4.5 Results and Discussion

The potential energy curves calculated by CNDO/S are shown in Figures 4.1 to 4.4. The electronic charge density differences between the excited electronic states and the reference state are shown in Tables 4.1, 4.2, 4.3



$R_{min}\,(^3A_1) = 2.65$ Å
$R_{min}\,(^3A_2) = 2.75$ Å
$E_{min}\,(^3A_1) = 5.30$ eV
$E_{min}\,(^3A_2) = 5.44$ eV
$\Delta E\;\;(^3A_1) = 3.20$ eV
$\Delta E\;\;(^3A_2) = 3.10$ eV

Fig. 4.1a Benzene-C_2 Pariser Triplets, Resting Model 1

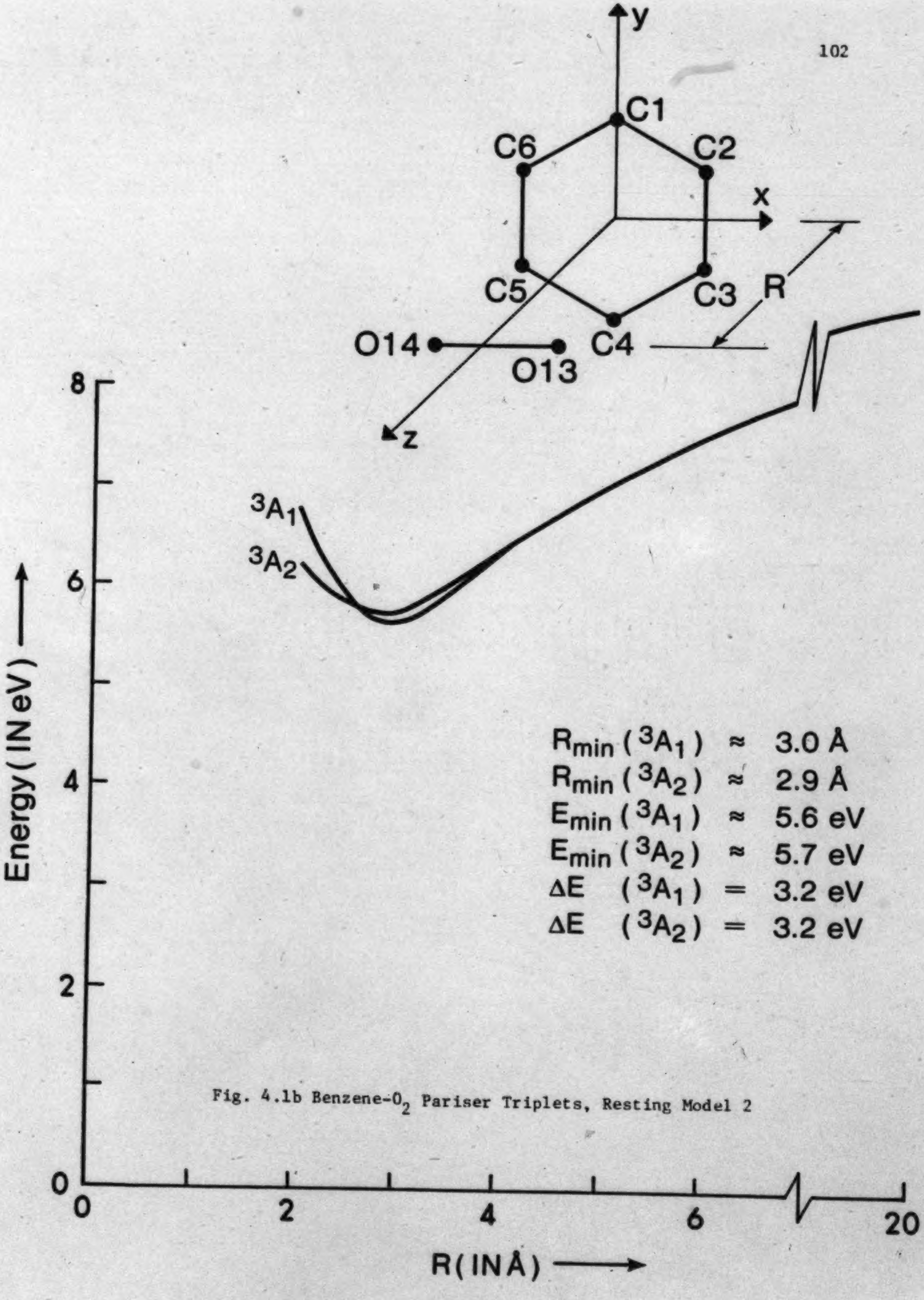


Fig. 4.1b Benzene-O_2 Pariser Triplets, Resting Model 2

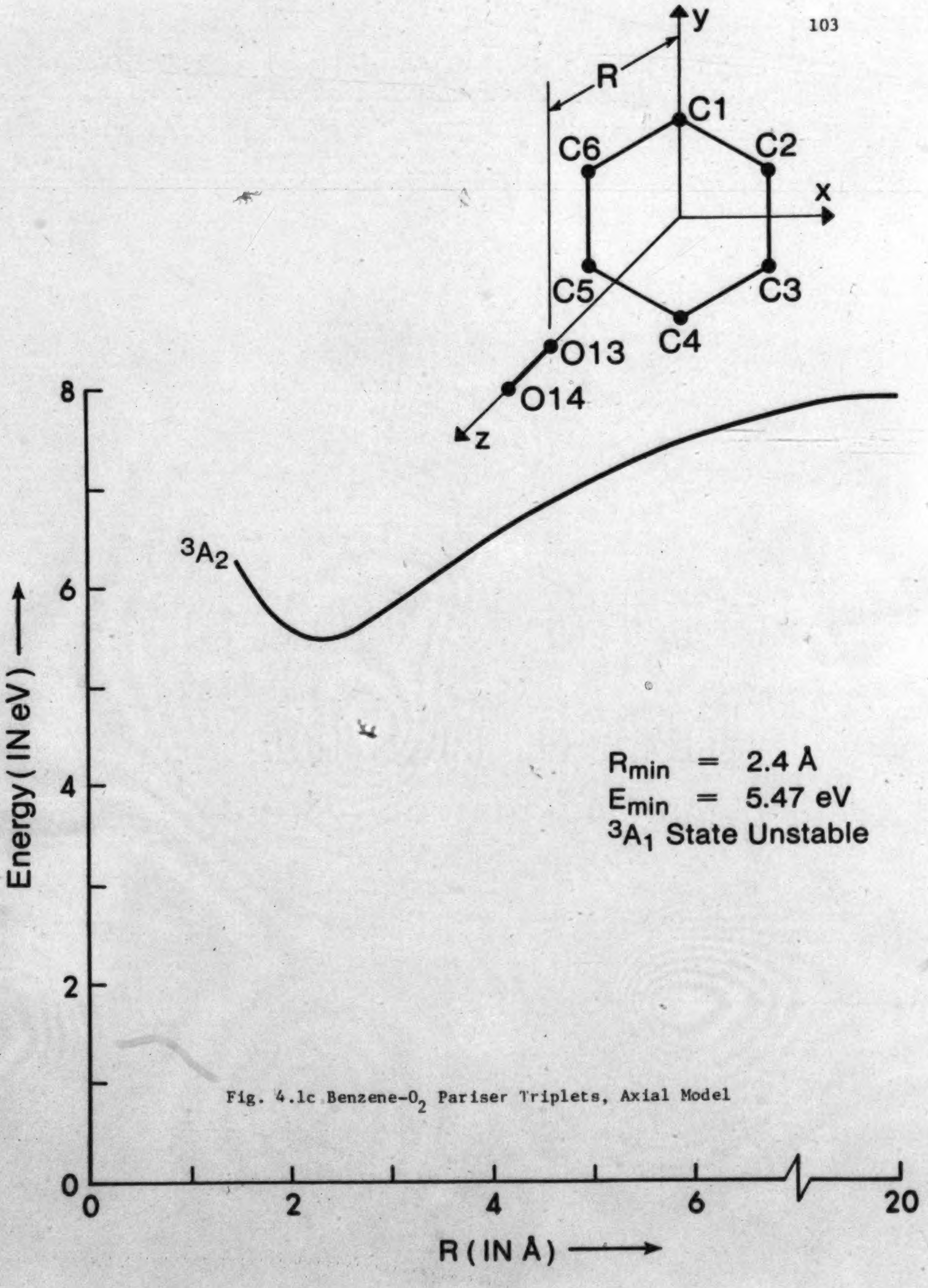


Fig. 4.1c Benzene-O_2 Pariser Triplets, Axial Model

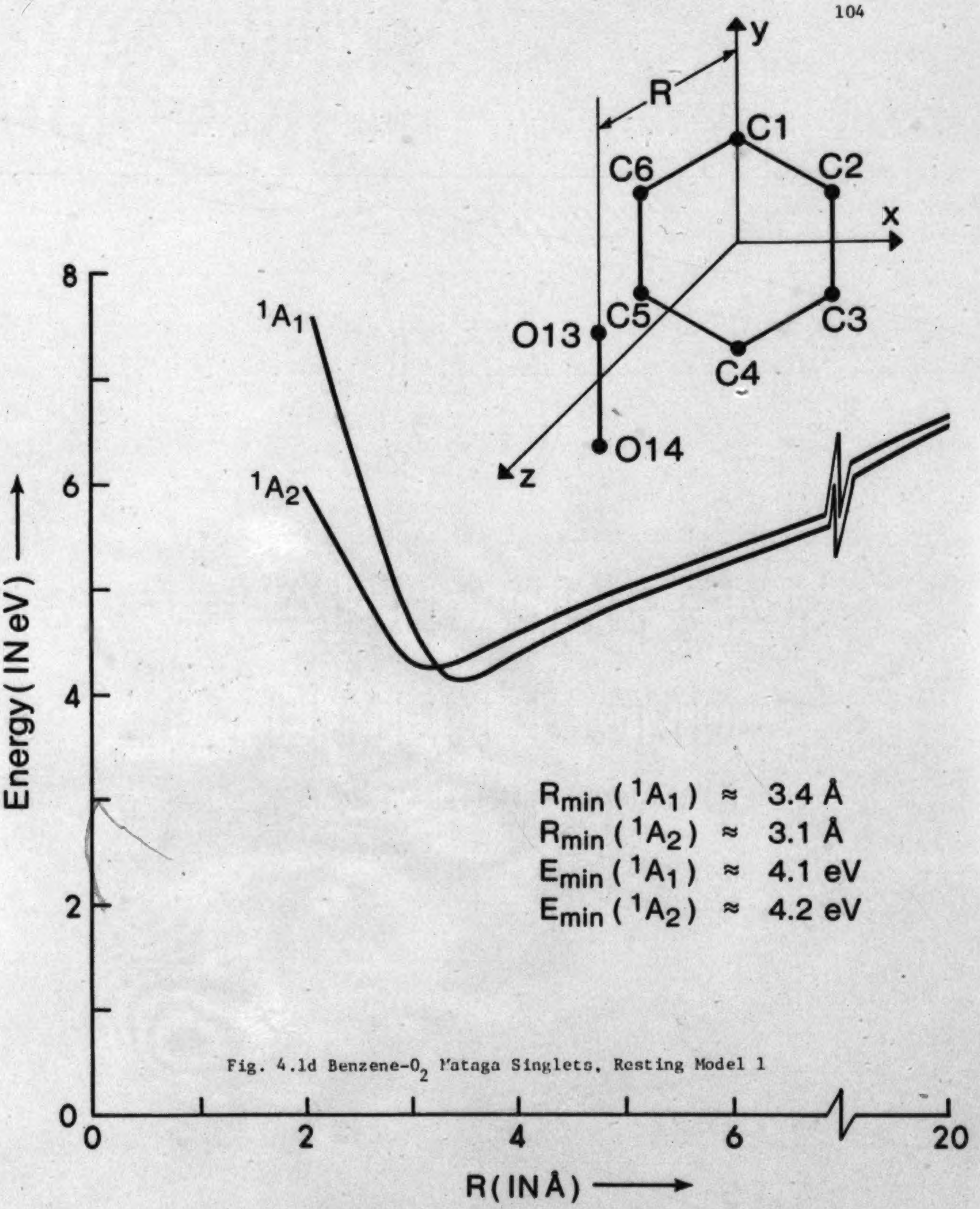


Fig. 4.1d Benzene-O_2 Mataga Singlets, Resting Model 1

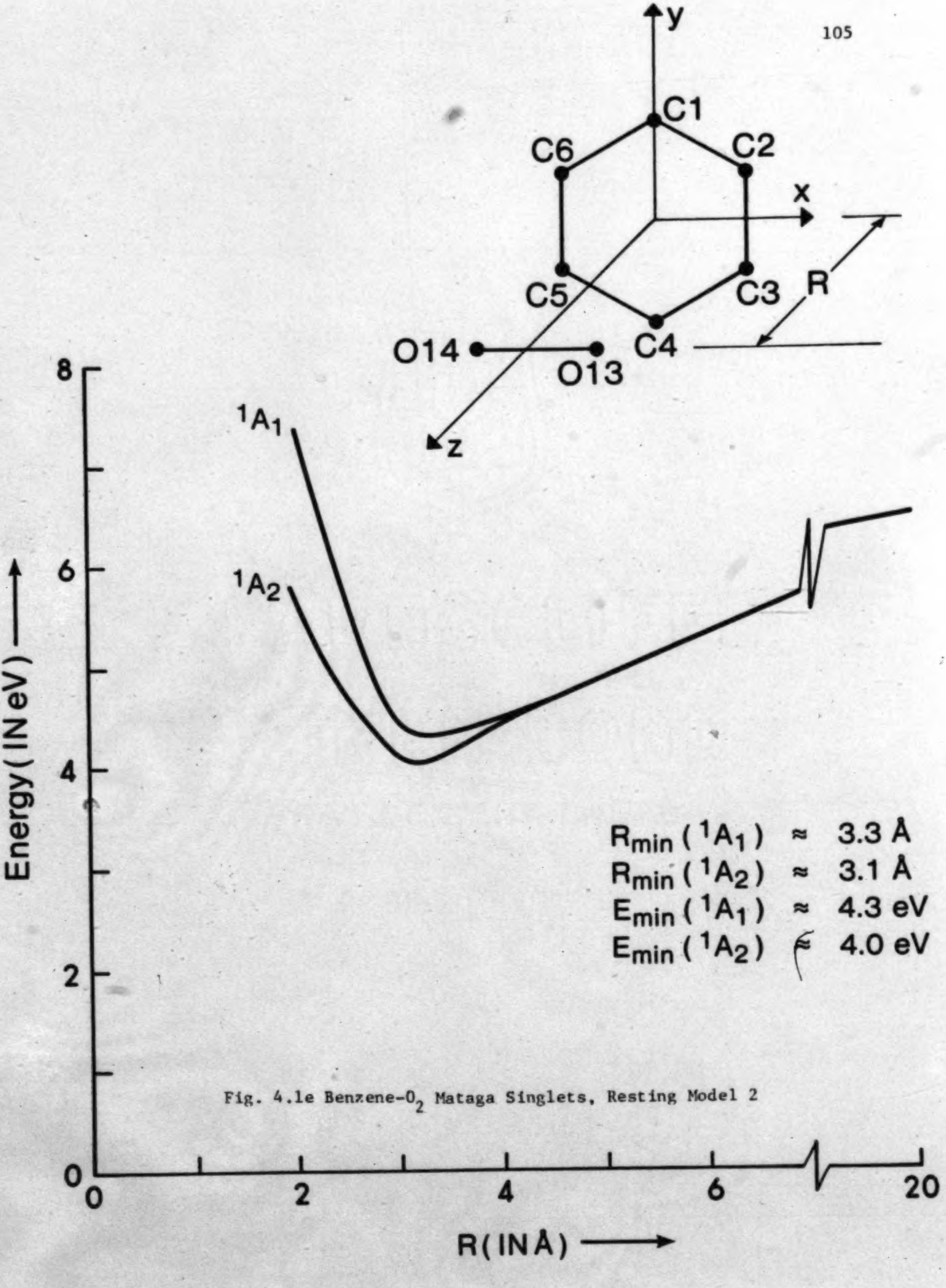


Fig. 4.1e Benzene-O_2 Mataga Singlets, Resting Model 2

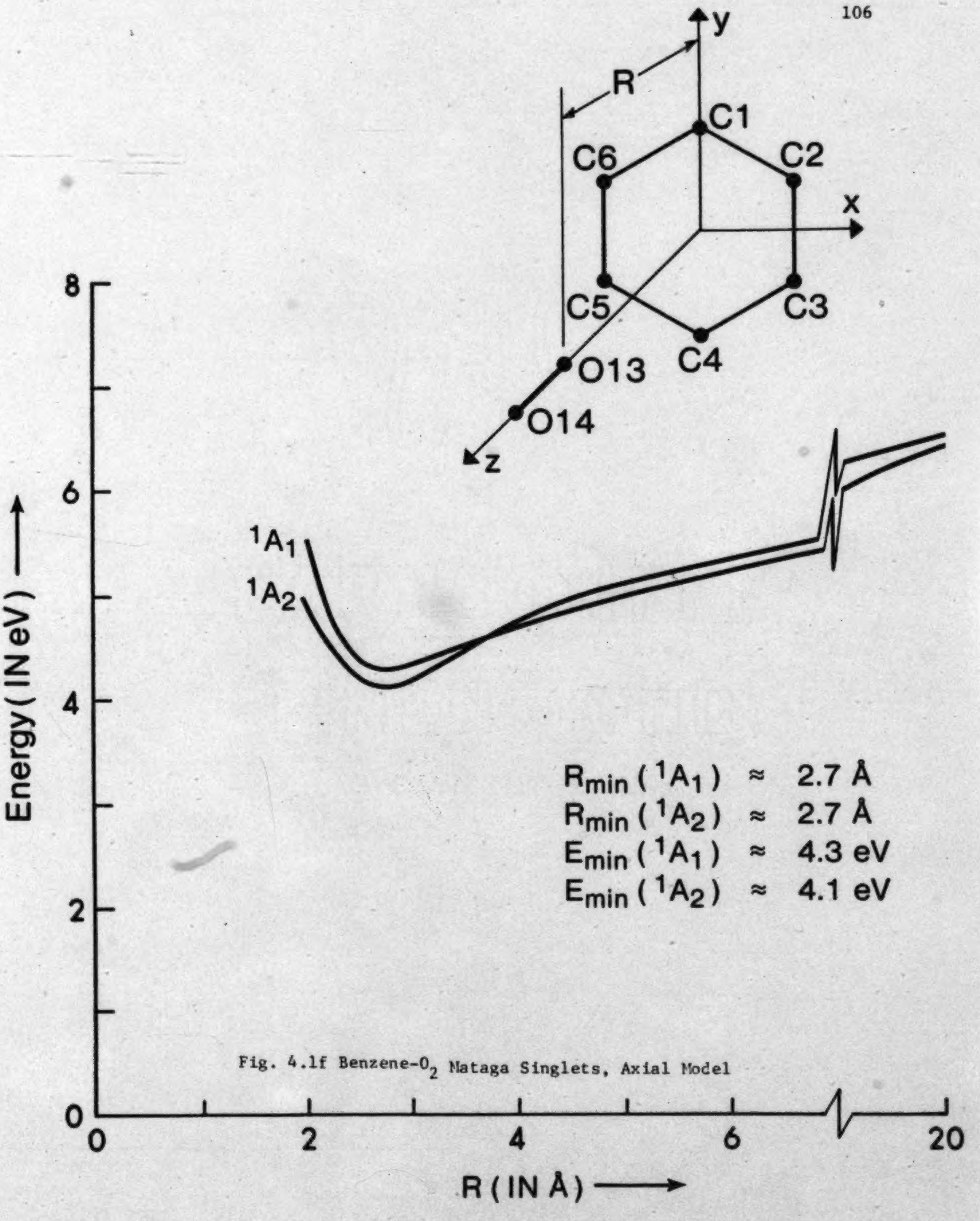


Fig. 4.1f Benzene-O_2 Mataga Singlets, Axial Model

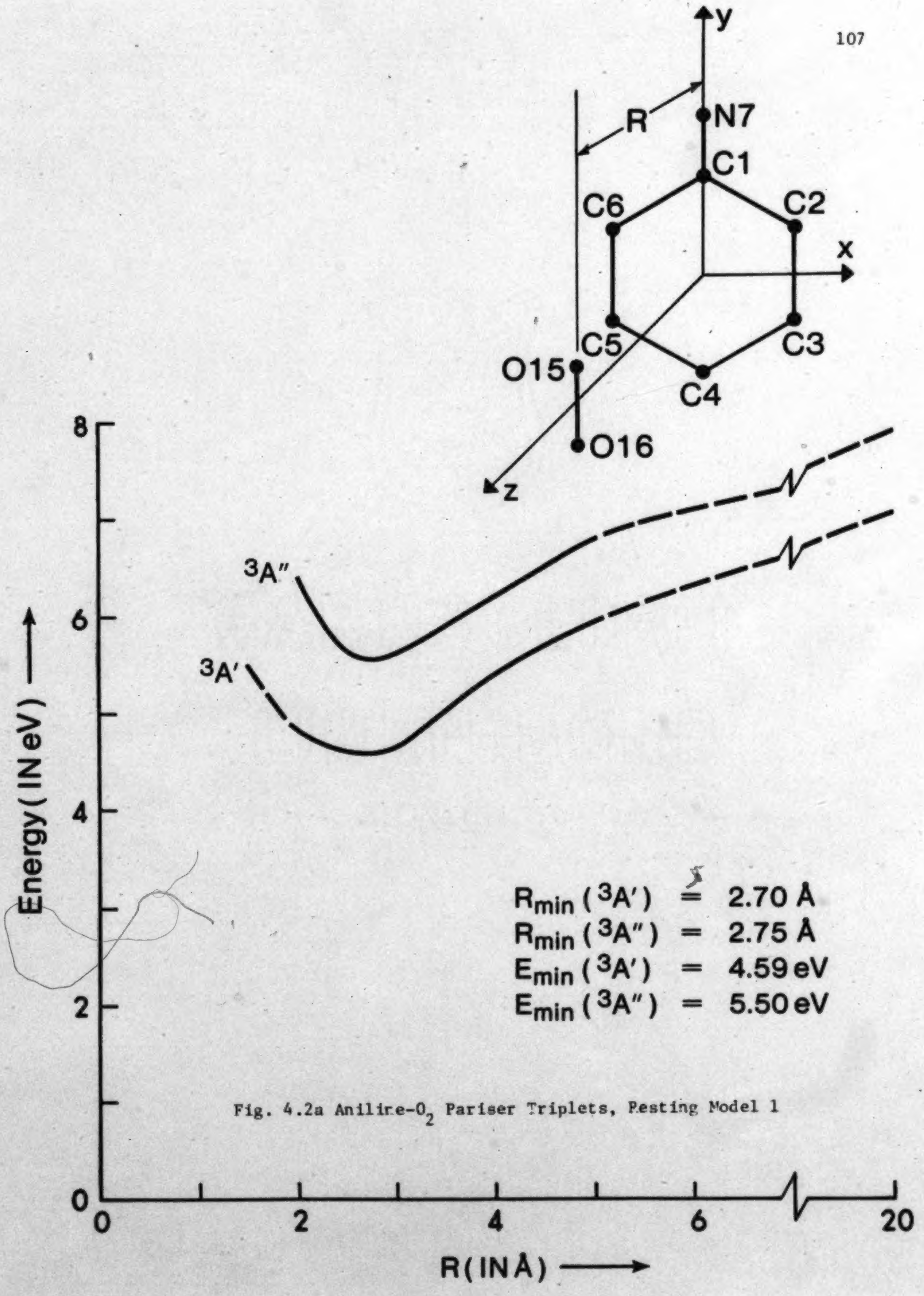


Fig. 4.2a Aniline-O_2 Pariser Triplets, Resting Model 1

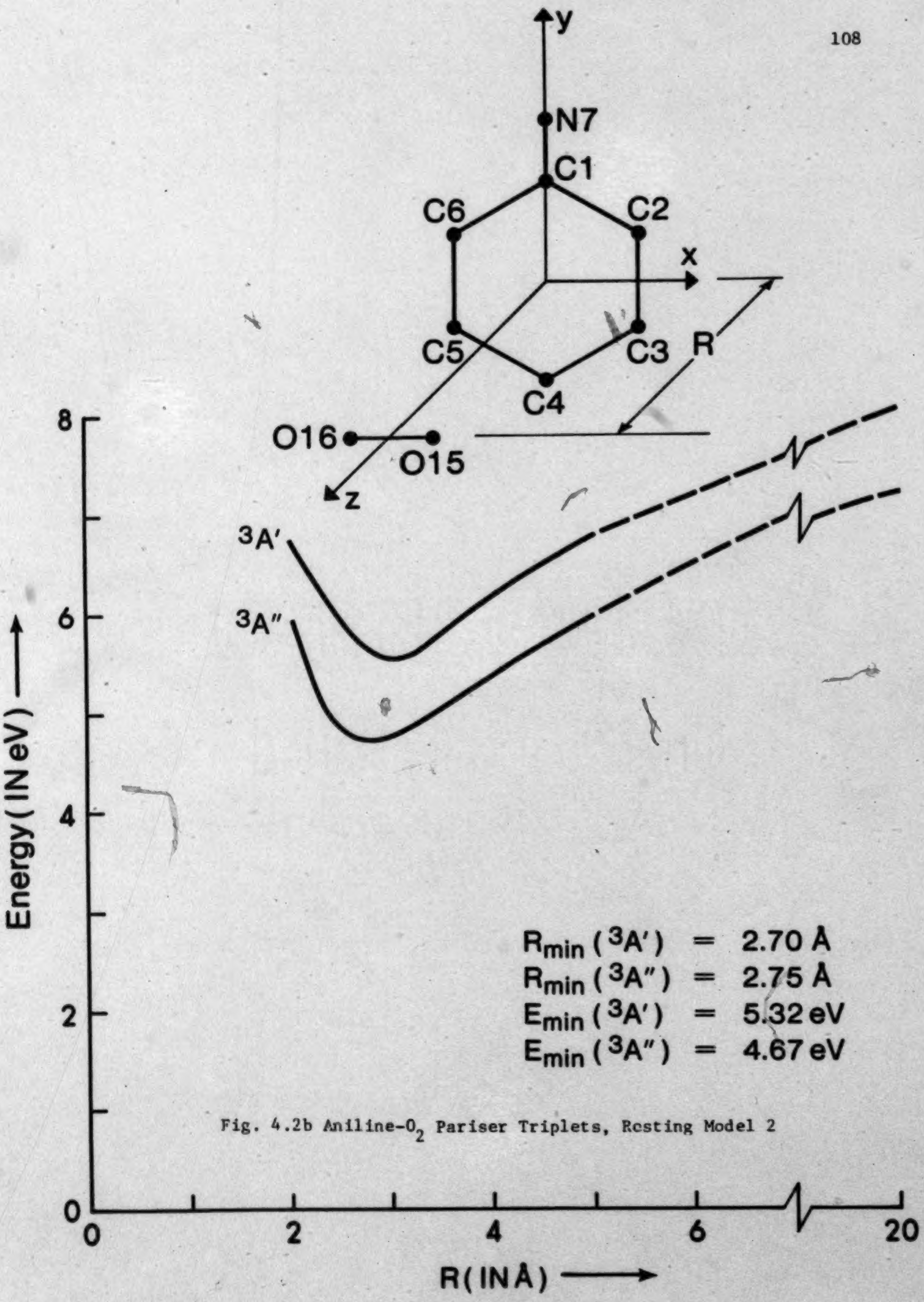


Fig. 4.2b Aniline-O_2 Pariser Triplets, Resting Model 2

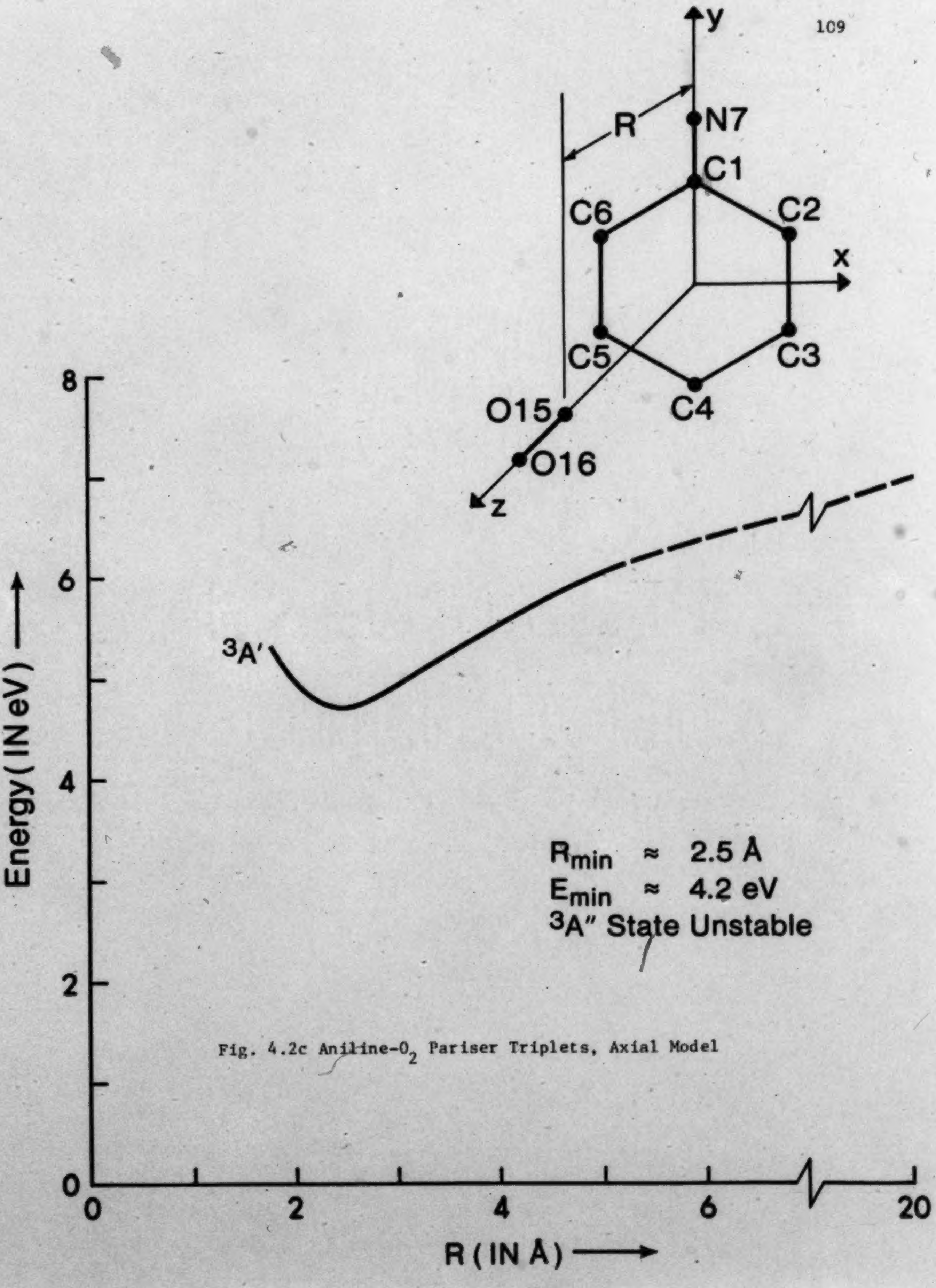


Fig. 4.2c Aniline-O_2 Pariser Triplets, Axial Model

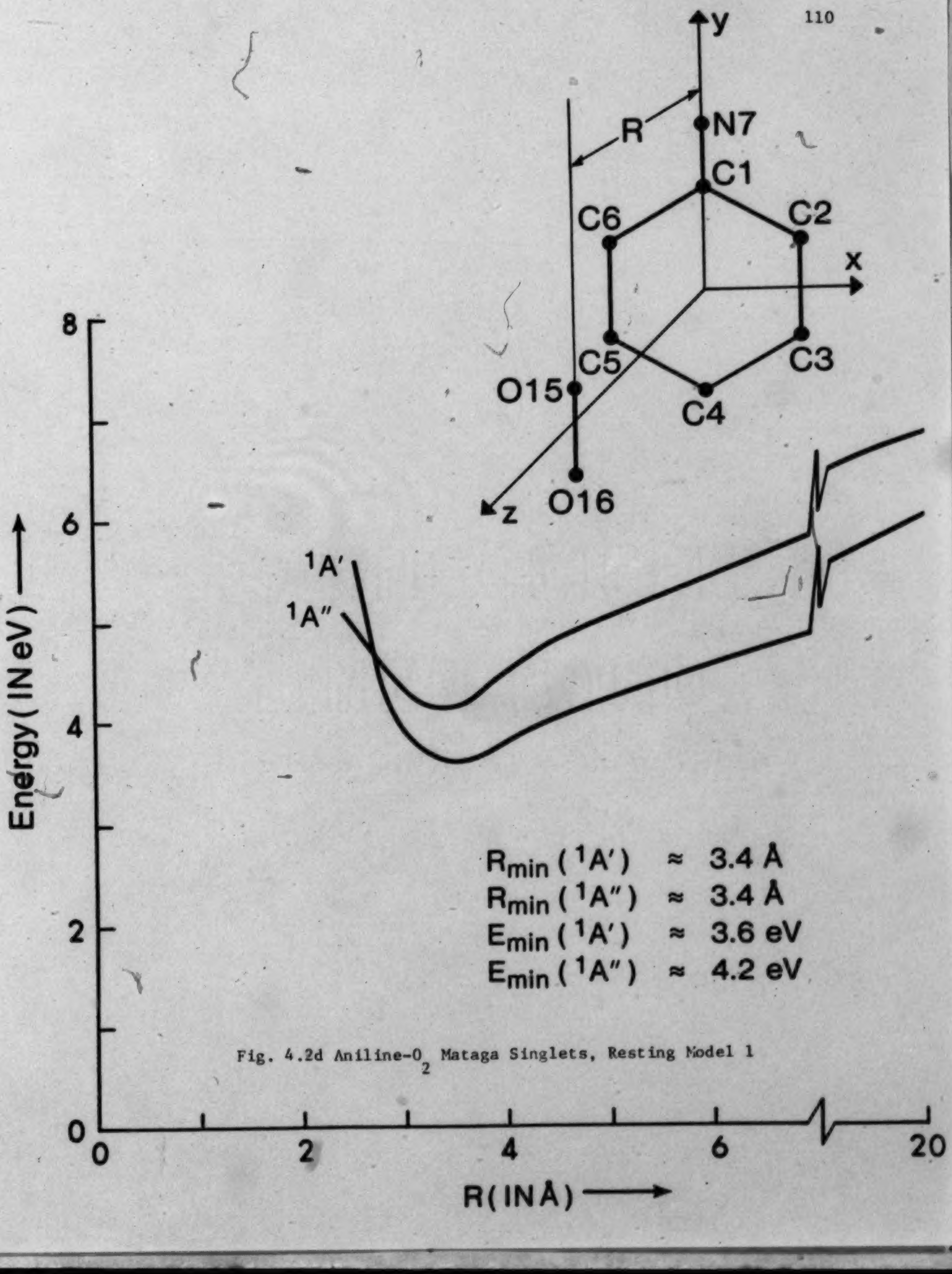


Fig. 4.2d Aniline-O_2 Mataga Singlets, Resting Model 1

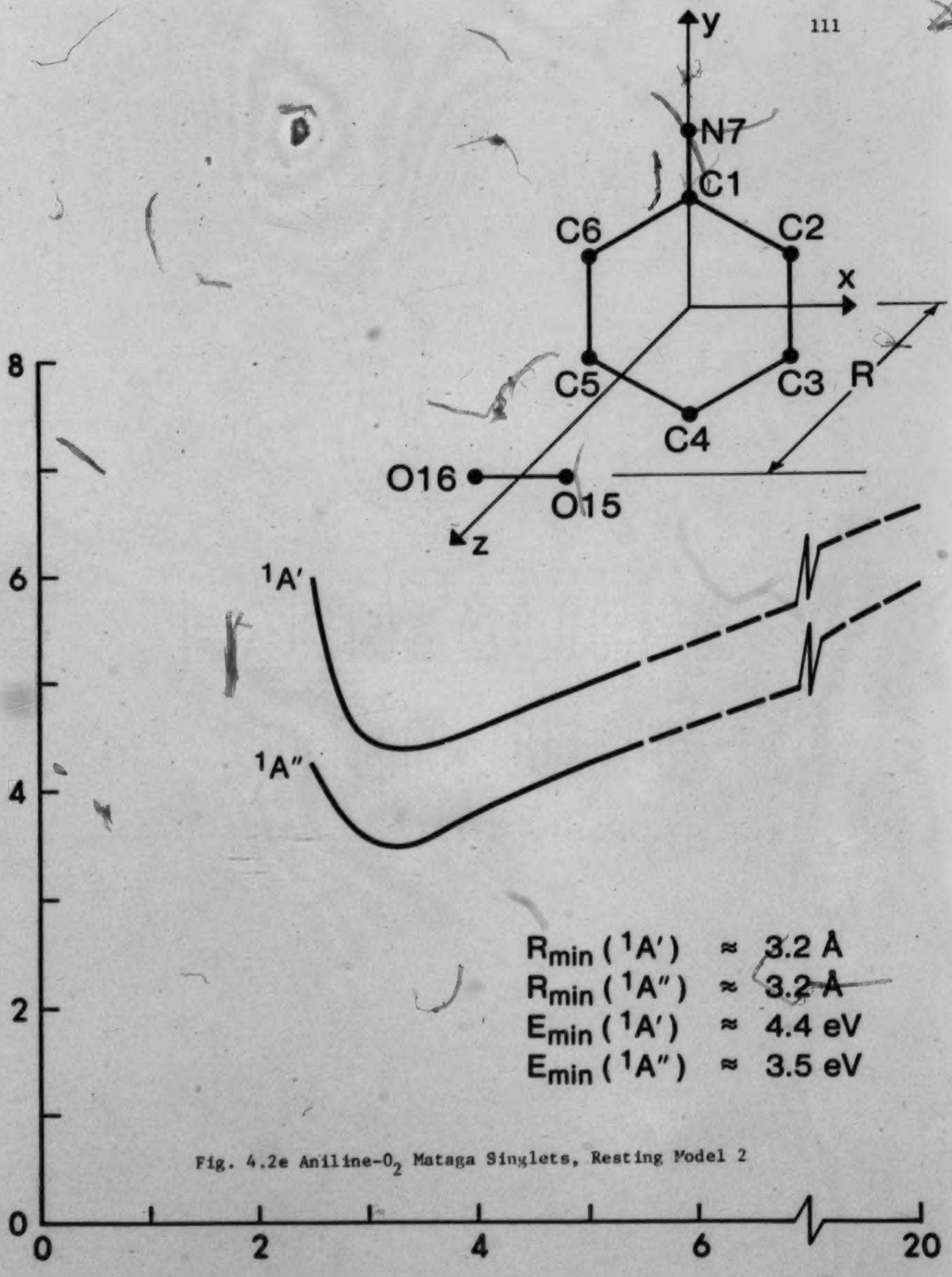


Fig. 4.2e Aniline-O_2 Mataga Singlets, Resting Model 2

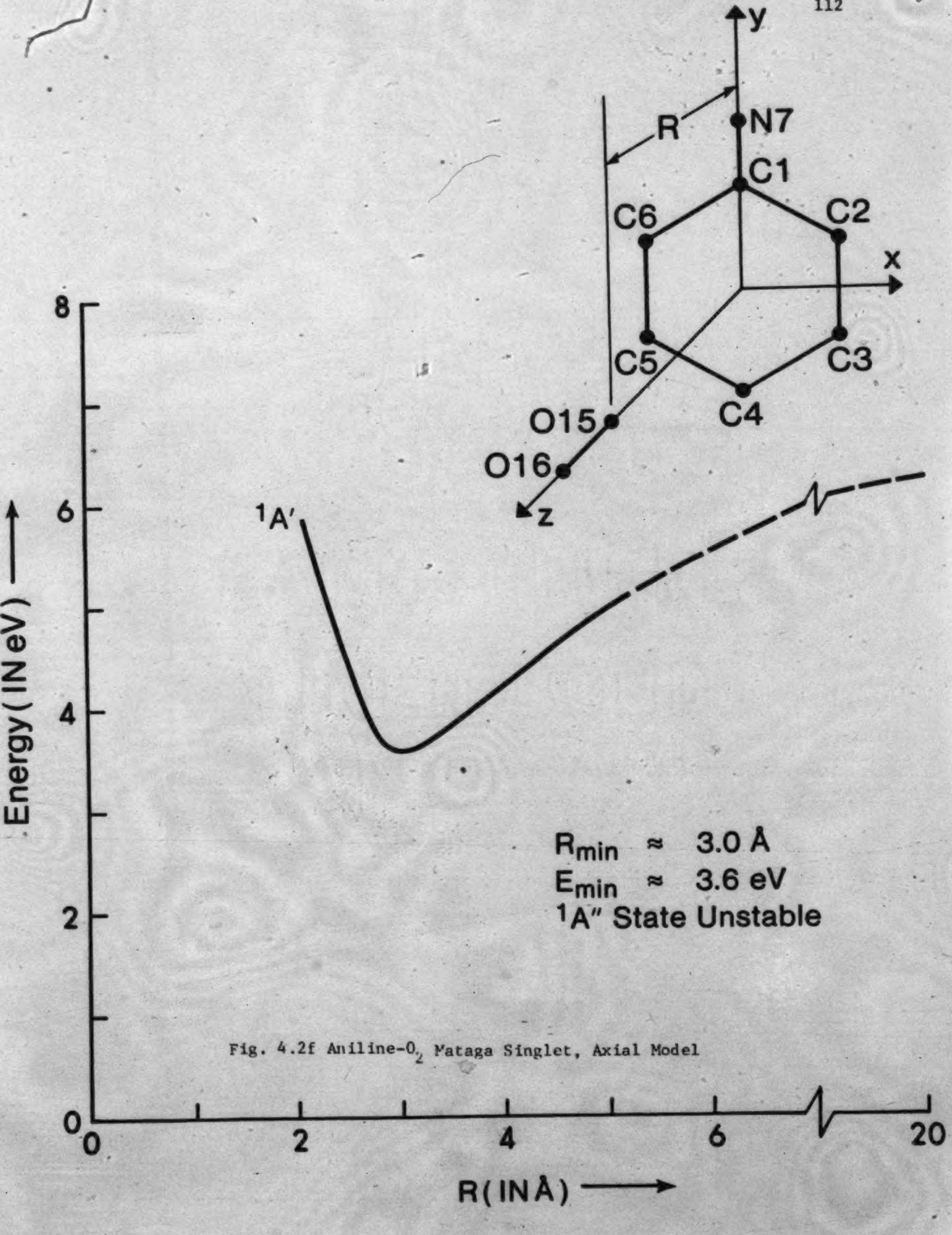


Fig. 4.2f Aniline-O_2 Mataga Singlet, Axial Model

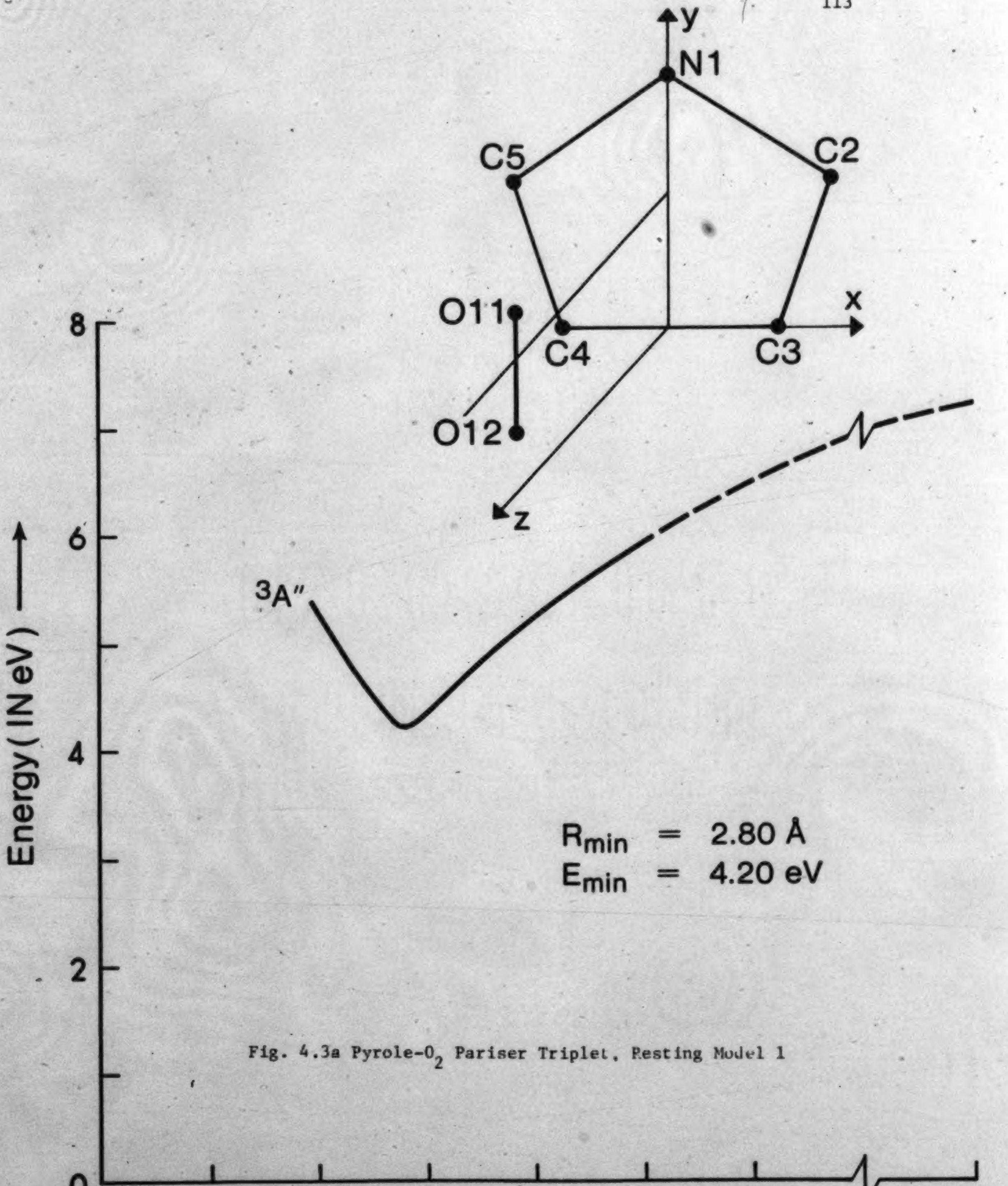


Fig. 4.3a Pyrole-0_2 Pariser Triplet, Resting Model 1

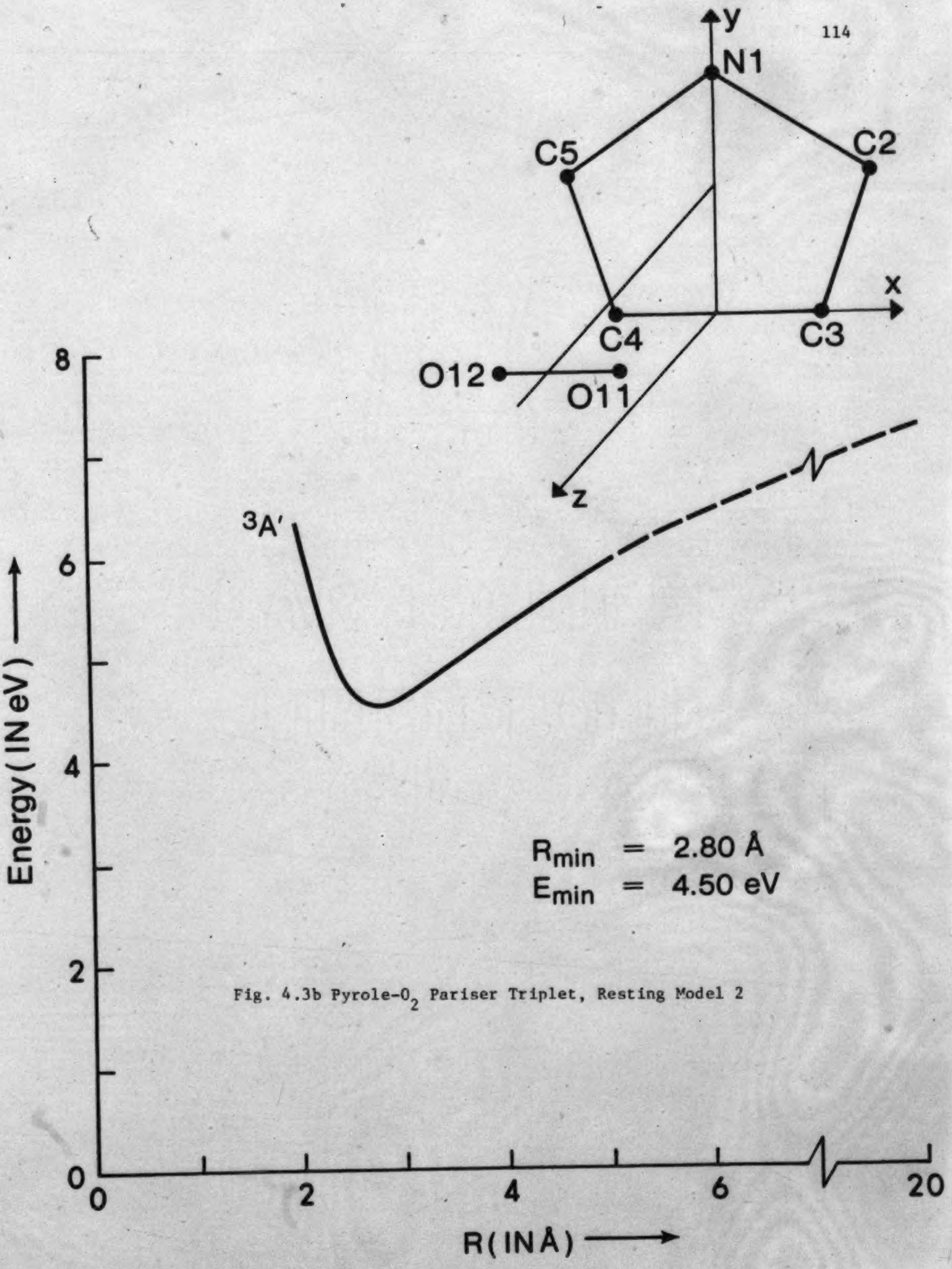


Fig. 4.3b Pyrole-O_2 Pariser Triplet, Resting Model 2

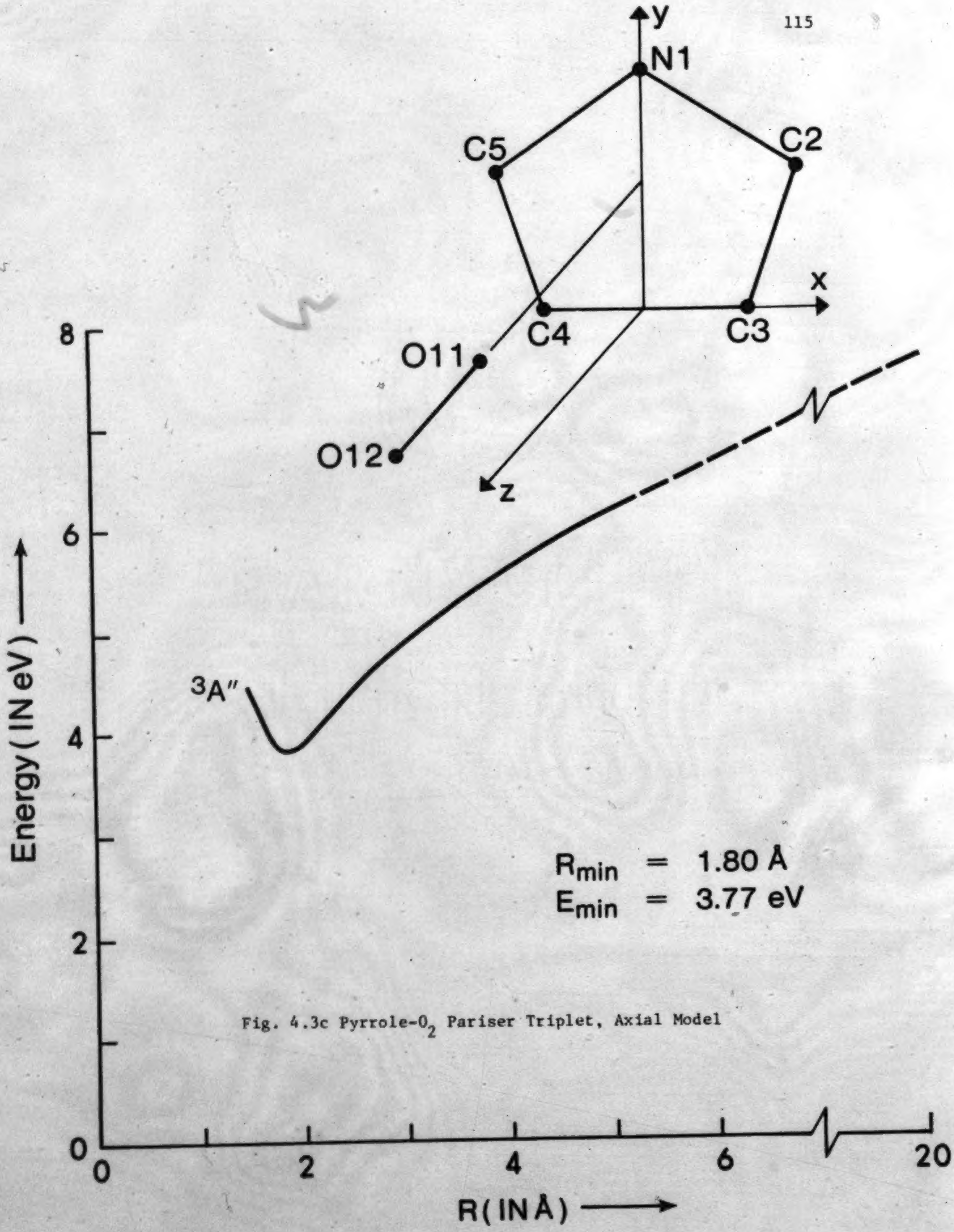


Fig. 4.3c Pyrrole-O_2 Pariser Triplet, Axial Model

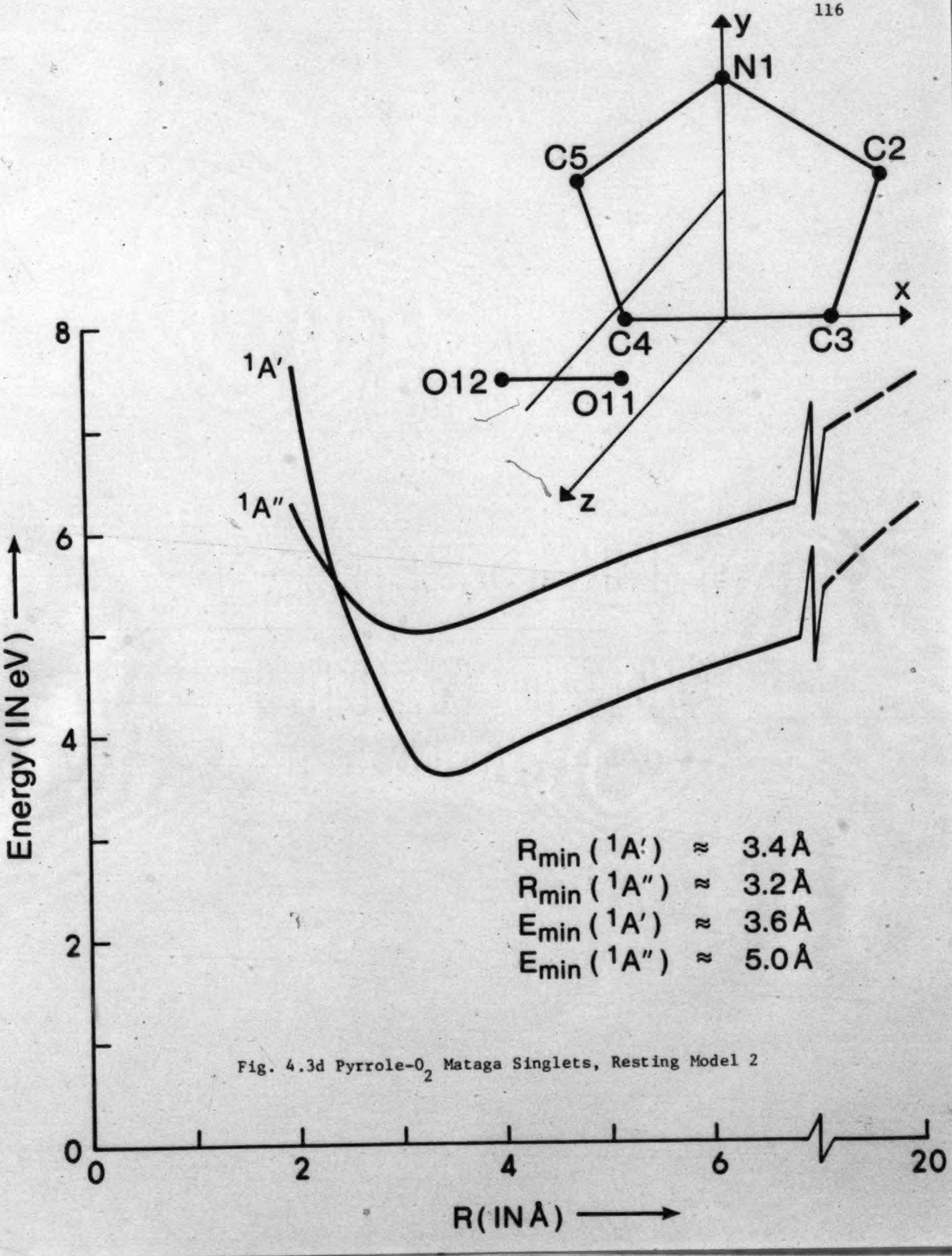


Fig. 4.3d Pyrrole-O_2 Mataga Singlets, Resting Model 2

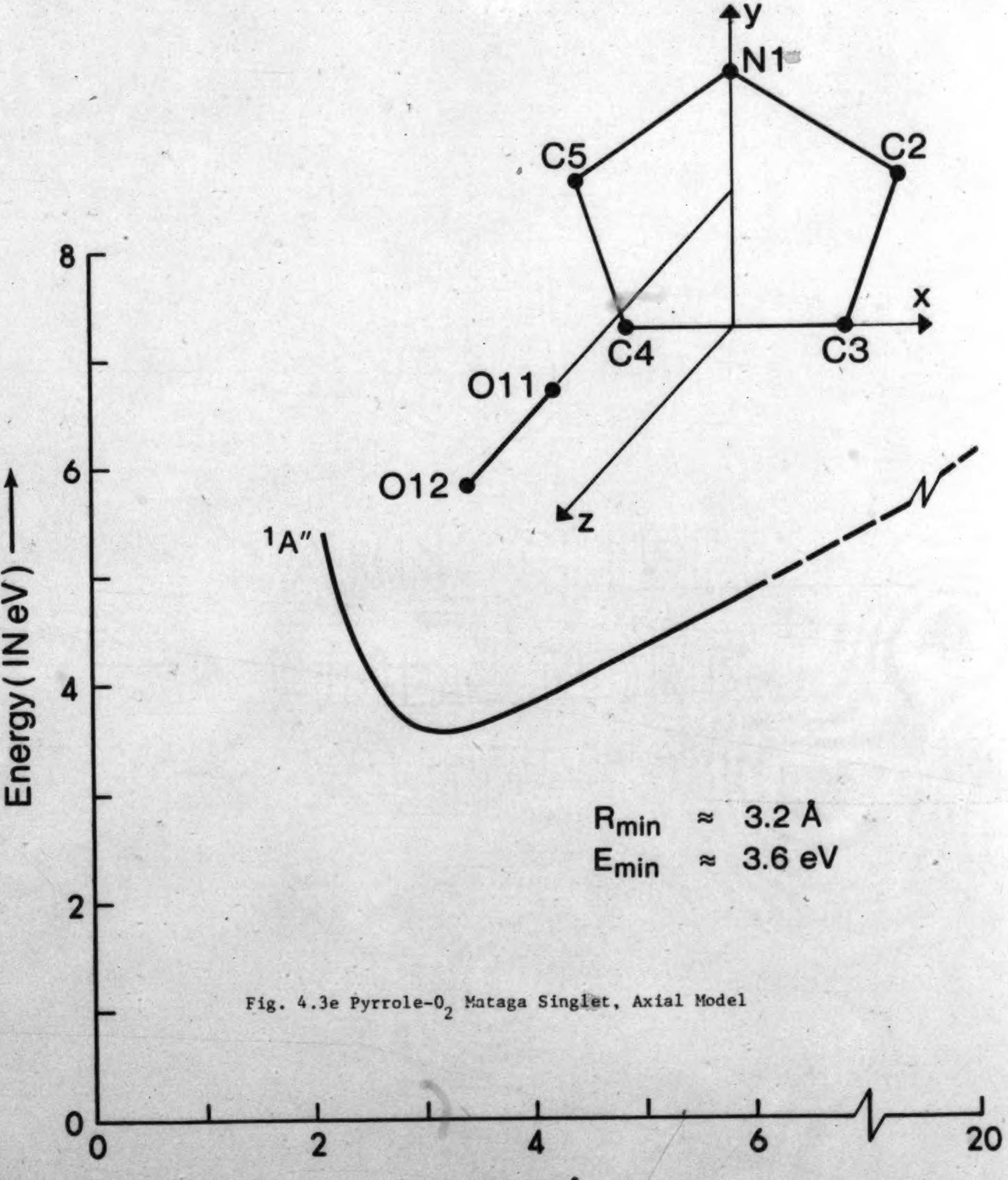


Fig. 4.3e Pyrrole-O_2 Mataga Singlet, Axial Model

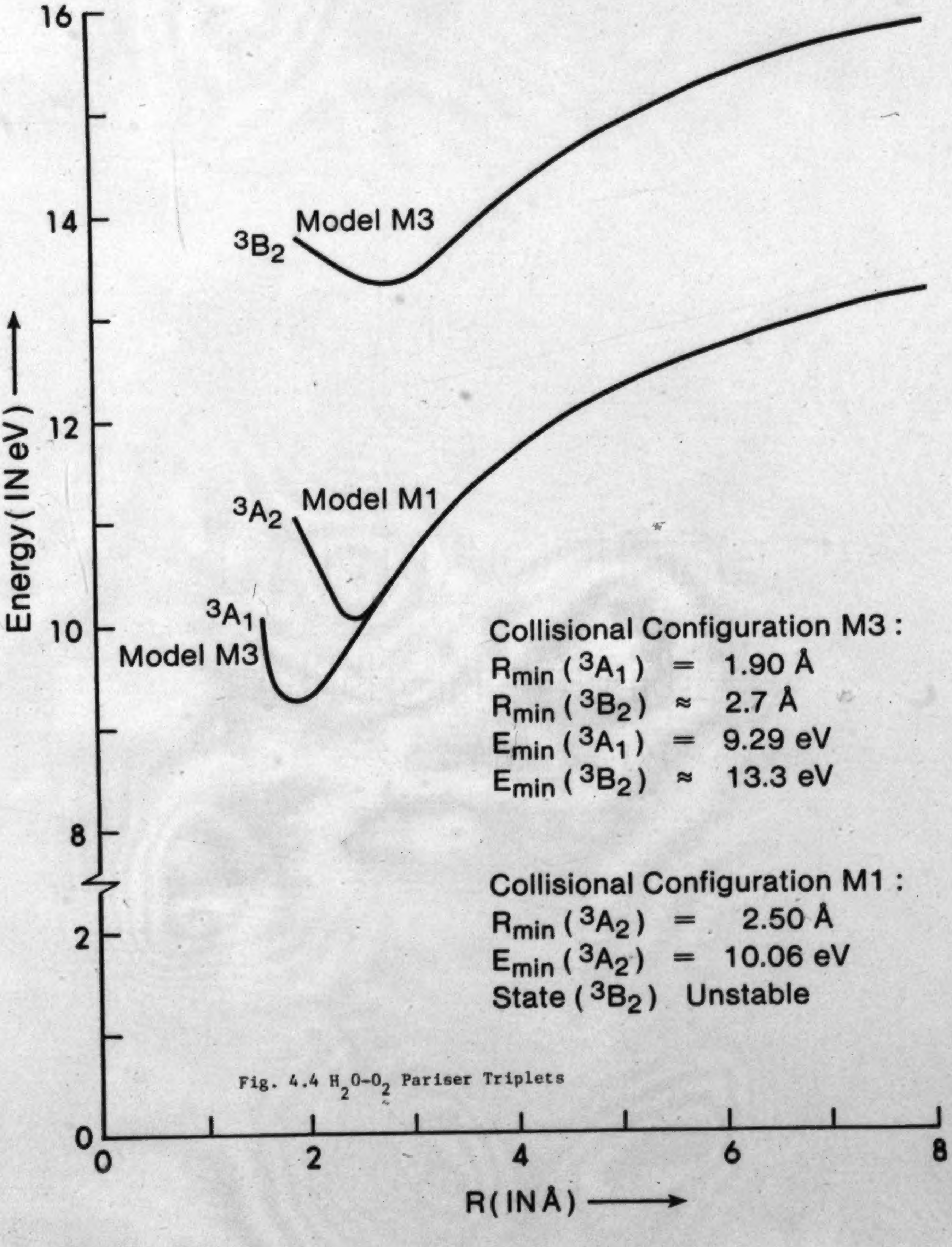


Fig. 4.4 H_2O-O_2 Pariser Triplets

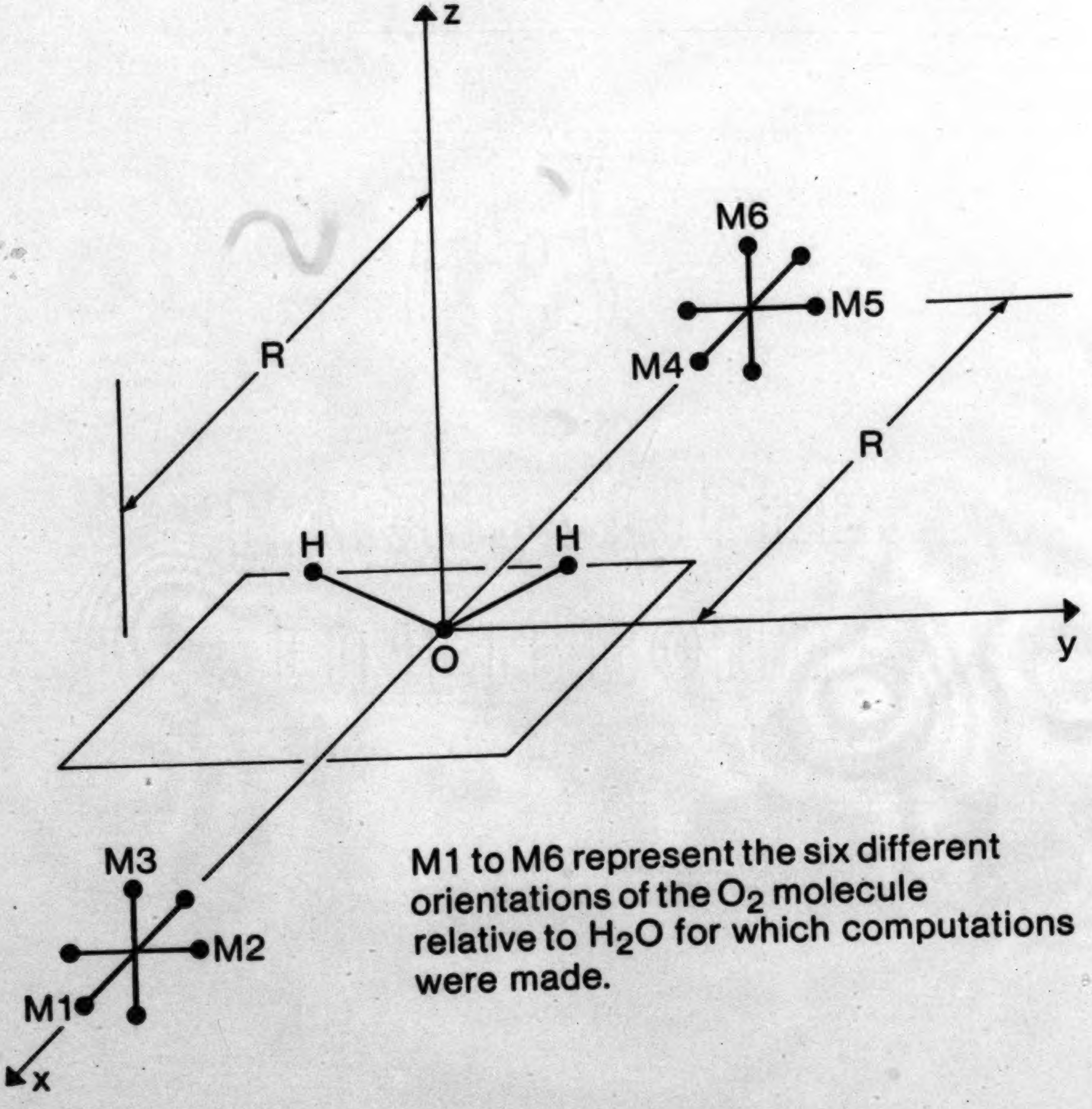

z
R
M6
M5
M4
R
H
H
O
y
M3
M2
M1
x
M1 to M6 represent the six different orientations of the O_2 molecule relative to H_2O for which computations were made.

Fig. 4.5 Configurations of the H_2O-O_2 Complex for which Computations were Carried Out

and 4.4.

The potential energy curves for both Mataga singlets and Pariser triplets - obtained for each molecular complex in the various collisional geometries and shown in Figures 4.1 to 4.4 correspond to the contact CT states formed after absorption. These potential energy curves correspond to the CT Franck-Condon states [119,120]. This follows from the fact that they are calculated by holding all internal coordinates fixed with only the collisional parameter R varying - a condition which describes a vertical Franck-Condon transition.

As mentioned in Chapter II, the CT theory outlined therein applies strictly speaking, to complexes in the vapor phase. Furthermore, since the CNDO/S results obtained in this work are for one-to-one associations, these results also are applicable to the vapor phase. Unfortunately however, the only experimental work done in the vapor phase is that by Birks *et.al.* [126] on the benzene-oxygen contact CT complex. Moreover, Tsubomura and Mulliken were unable to extend their work to obtain peak absorption wavelengths to any great accuracy. Heidt *et.al.* also did not establish an experimental value for the peak absorption wavelength in the H_2O-O_2 complex.

The CNDO/S potential curves shown are drawn relative to a reference closed-shell structure. Hence, in this case the curves represent the energy difference between the excited states and the reference closed-shell electronic state.

The potential energy minima calculated correspond approximately to the peak absorption wavelengths that can be expected in experimental measurements. As mentioned above, except for the benzene-oxygen spectrum, experimental peak absorption wavelengths are, at present, unavailable.

Table 4.1a Charge Transfer Behaviour of Benzene-Oxygen Stable Pariser Triplets

	Axial Model	Resting Model 1		Resting Model 2	
	R = 2.4Å	R = 2.65Å	R = 2.75Å	R = 3Å	R = 3Å
	State $^3A_2$	State $^3A_1$	State $^3A_2$	State $^3A_1$	State $^3A_2$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
C1	0.005	-0.306	0.009	0.000	- 0.331
C2	-0.218	-0.075	-0.242	-0.245	- 0.080
C3	-0.218	-0.075	-0.242	-0.245	- 0.080
C4	0.005	-0.306	0.009	0.000	- 0.331
C5	-0.218	-0.075	-0.242	-0.245	- 0.080
C6	-0.218	-0.075	-0.242	-0.245	- 0.080
O13	0.434	0.456	0.476	0.489	0.492
O14	0.427	0.456	0.476	0.489	0.492

Table 4.1b Charge Transfer Behaviour of Benzene-Oxygen Stable Mataga Singlets

	Axial Model		Resting Model 1		Resting Model 2	
	R = 3Å		R = 3Å		R = 3Å	
	State $^1A_1$	State $^1A_2$	State $^1A_1$	State $^1A_2$	State $^1A_1$	State $^1A_2$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
C1	-0.332	0.001	-0.321	0.006	0.000	-0.332
C2	-0.083	-0.248	-0.080	-0.248	-0.240	-0.078
C3	-0.083	-0.248	-0.080	-0.248	-0.240	-0.079
C4	-0.332	0.001	-0.321	0.006	0.000	-0.332
C5	-0.083	-0.248	-0.080	-0.248	-0.240	-0.078
C6	-0.083	-0.248	-0.080	-0.248	-0.240	-0.079
O13	0.500	0.496	0.481	0.489	0.481	0.489
O14	0.495	0.494	0.481	0.489	0.481	0.489

Table 4.2a Charge Transfer Behaviour of Aniline-Oxygen Stable Pariser Triplets

	Axial	Resting Model 1		Resting Model 2	
	R = 2.75Å	R = 2.75Å	R = 2.75Å	R = 2.60Å	R = 2.75Å
	State $^3A'$	State $^3A'$	State $^3A''$	State $^3A'$	State $^3A''$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
C1	-0.198	-0.158	0.005	0.002	-0.198
C2	-0.122	-0.110	-0.241	-0.222	-0.101
C3	-0.039	0.027	-0.232	-0.211	-0.016
C4	-0.256	-0.210	0.008	0.001	-0.247
C5	-0.039	-0.027	-0.232	-0.211	-0.016
C6	-0.122	-0.110	-0.241	-0.222	-0.101
N7	-0.210	-0.208	-0.003	-0.003	-0.209
015	0.498	0.427	0.467	0.433	0.444
016	0.487	0.423	0.468	0.433	0.444

Table 4.2b Charge Transfer Behaviour of Aniline-Oxygen Stable Mataga Singlets

	Axial Model	Resting Model 1		Resting Model 2	
	R = 3Å	R = 3Å	R = 3Å	R = 3Å	R = 3Å
	State $^1A'$	State $^1A'$	State $^1A''$	State $^1A'$	State $^1A''$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
C1	-0.214	-0.204	0.006	0.000	-0.215
C2	-0.117	-0.113	-0.254	-0.248	-0.113
C3	-0.043	-0.040	-0.240	-0.233	-0.038
C4	-0.265	-0.250	0.008	-0.000	-0.264
C5	-0.043	-0.040	-0.240	-0.233	-0.038
C6	-0.117	-0.113	-0.254	-0.248	-0.113
N7	-0.196	-0.196	0.001	-0.000	-0.198
O15	0.500	0.478	0.487	0.482	0.490
O16	0.500	0.476	0.487	0.482	0.490

Table 4.3a Charge Transfer Behaviour of Pyrrole-Oxygen Stable Pariser Triplets

	Axial Model	Resting Model 1	Resting Model 2
	R = 1.8Å	R = 2.8Å	R = 2.8Å
	State $^3A''$	State $^3A''$	State $^3A'$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
N1	-0.002	-0.001	-0.001
C2	-0.152	-0.326	-0.324
C3	-0.063	-0.143	-0.141
C4	-0.063	-0.143	-0.141
C5	-0.152	-0.326	-0.324
011	0.377	0.467	0.465
012	0.061	0.471	0.465

Table 4.3b Charge Transfer Behaviour of Pyrrole-Oxygen Stable Mataga Singlets

	Axial Model	Resting Model 2	
	R = 3.0Å	R = 3.0Å	R = 3.0Å
	State $^1A''$	State $^1A'$	State $^1A''$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
N1	0.000	-0.000	-0.413
C2	-0.348	-0.331	-0.009
C3	-0.148	-0.139	-0.266
C4	-0.148	-0.139	-0.266
C5	-0.348	-0.331	-0.009
011	0.499	0.470	0.481
012	0.492	0.470	0.481

Table 4.4 Charge Transfer Behaviour of H_2O-O_2 Stable Pariser Triplets

	Model M1	Model M_3	
	R = 2.5Å	R = 1.85 Å	R = 3Å
	State $^3A_2$	State $^3A_1$	State $^3B_2$
Atom	Electron Density Transferred	Electron Density Transferred	Electron Density Transferred
01	-0.848	-0.898	-0.560
H2	0.000	0.000	-0.026
H3	0.000	0.000	-0.026
04	0.444	0.449	0.306
05	0.403	0.449	0.306

It should be noted here that the ground electronic states of O_2 and the donor molecules investigated are triplet and singlet states respectively. As the oxygen-donor pair is a very weak complex, or a "contact pair", the wavefunction of the ground state of this pair can be represented by the fully antisymmetrized product of those for the individual molecules, $\Psi(^3\Sigma_g^-)$ and $\Psi(^1A)$ [49]. The overall ground state for the complex is therefore a triplet. The CT state may be a triplet or a singlet depending on the relative spins of the two electrons in the half-filled molecular orbitals. The experimentally observed CT spectra are those which correspond to transitions between the ground state and the triplet CT excited state. These experimentally observed spectra are therefore spin-allowed [49].

For example, the CT state observed experimentally in a mixture of O_2 and benzene may be attributed to the following transition:

$$\mathrm{Bz}\ldots\pi^2\psi(E_1a)\pi^2\psi(E_1b);O_2\ldots\pi^*(2p_x)\pi^*(2p_y)\rightarrow\mathrm{Bz}\ldots\pi^2\psi(E_1a)\pi\psi(E_1b);O_2\ldots$$
$$(\pi^*)^2(2p_x)\pi^*(2p_y) \qquad (4.17)$$

where the superscripts represent orbital occupancies and the starred orbitals are antibonding molecular orbitals.

Similar $\pi\rightarrow\pi^*$ transitions result in the charge-transfer states of aniline and pyrrole with O_2. The H_2O-O_2 contact states ($^3A_1$ and $^3A_2$ in Figure 4.4) account for the experimentally observed spectrum and are due to transitions from a nonbonding H_2O molecular orbital (centred on the O atom).

The CT state will be a singlet or a triplet depending on the relative spins of the electrons in the half filled orbitals $\pi\psi(E_1b)$ and $\pi^*(2p_y)$ on the right hand side of (4.17).

The reference closed shell configuration in the CNDO/S calculations in this work corresponds to double occupancy in the π^* molecular orbital of O_2 and hence the CT state corresponds to the following transition

$$\mathrm{Bz}\ldots\pi^2\psi(E_1a)\pi^2\psi(E_1b);O_2\ldots(\pi^*)^2(2p_x)\rightarrow\mathrm{Bz}\ldots\pi^2\psi(E_1a)\pi\psi(E_1b);O_2\ldots(\pi^*)^2(2p_x)\pi^*(2p_y) \tag{4.18}$$

Since the final electronic configuration in both these instances((4.17) and (4.18)) is identical and since the donor electron comes from the same orbital of the donor molecule, the difference in the initial configurations is not very consequential especially in comparison to the charge transfer stabilization of the excited state [36]. Furthermore, as an initial approximation this difference was compensated for by adding to the CNDO/S potential energies the value of the singlet-triplet splitting of the O_2 molecule (0.97ev). The potential energy curves shown are drawn after this correction has been made.

The Pariser triplet curves obtained describe accurately the experimental results (both quantitatively and qualitatively). Mataga singlets and triplets calculated also describe the charge-transfer stabilization of the complexes. The calculated Mataga triplets were always lower than the corresponding Mataga singlets in accordance with Hund's Rule.

It appears, however, that the Mataga Approximation, although reproducing the qualitative Charge-Transfer stabilization of these complexes quite well, consistently underestimates the energies. It is important to keep this fact in mind in any comparison between the singlet and triplet curves.

The Pariser triplet curves obtained are in agreement quantitatively with all the experimental data available to date and will form the basis of comparison between theory and experiment below.

4.5.1 Electron Affinities and Ionization Potentials

The oxygen vertical electron affinity in these complexes can be deduced from the benzene-oxygen Pariser triplet curves. The ionization energy of the benzene $\psi(E_1a)$ and $\psi(E_1b)$ orbitals is well established as 9.24ev [16]. Using the fact that for CT complexes the asymptotic limit of energy is equal to the difference between the vertical ionization energy of the donor orbital and the vertical electron affinity of the acceptor orbital (as given by equation 2.37), this yields the value 0.57ev as the electron affinity for O_2. This compares favourably with the value of 0.67±0.2ev quoted by Birks [127].

The potential energy curves presented for the aniline-oxygen and pyrrole-oxygen complexes (Figures 4.2 and 4.3) have been extrapolated for values of R greater than 5Å. This was found to be necessary because SCF energy convergence was not obtained at values of $R > 5Å$ (oscillations of computed energy values were observed here). The extrapolations were made by using equation (2.37), the electron affinity calculated above (0.57ev) and the experimental values of the first ionization values of aniline (7.70ev) [16] and pyrrole (8.87ev) [128]. The extrapolations of the second CT states in these cases are much more uncertain because the second ionization energies for aniline and pyrrole were not available.

For the H_2O-O_2 complex, as for the benzene-O_2 complex such non-convergence problems were not encountered. From Table 4.4, it is seen that the $^3A_2$ and $^3A_1$ states in configurations M1 and M3 correspond to the donation of a lone-pair electron on the H_2O molecule to the O_2 antibonding m.o. The ionization energy for this m.o. is obtained from Figure 4.4, equation (2.37) and the value of electron affinity for O_2. The value of I thus deduced is 14.24ev, which compares reasonably well with the experimental value of 12.59ev quoted by Mulliken [16].

4.5.2 Energies of Formation from the Ionic Monomers

The energy of formation, ΔE, of a CT state from the corresponding ions of the donor and acceptor molecules (D^+ and A^-) is the difference between the asymptotic energy (as $R \to \infty$) of the state and the value of the potential energy minimum, E_{min}, for that state. These energies can be calculated for the complexes of benzene and H_2O, since here SCF convergence problems were not encountered for large R.

For the triplet contact CT states of the benzene-oxygen complex ΔE is between 3.1ev and 3.2ev depending on the species and the geometrical configuration. The exact values are given in Figures 4.2a and 4.2b . This compares very favourably with the experimental value of 2.9ev observed by Birks *et.al.* [126].

The corresponding energies of formation for the H_2O-O_2 complex can be obtained from Figure 4.4. These are 3.9, 2.1 and 2.2ev for the $^3A_1$, $^3A_2$ and $^3B_2$ states respectively. Unfortunately, experimental values for these energies are unavailable.

For the complexes of aniline and pyrrole, the theoretical energies of formation cannot be given. This follows from the fact that, as mentioned previously, the potential energy curves for $R \gtrsim 5\text{Å}$ have had to be extrapolated using experimental ionization potentials. The values that can be obtained from Figures 4.2 and 4.3 for these complexes, may however be regarded as semiemperical values, since the potential energy minima were calculated by CNDO/S.

4 .5.4 Charge-Transfer Nature of Computed States

The Charge-Transfer nature of the excited states computed is clearly revealed by the results in Tables 4.1 to 4.4. These tables give the calculated electron density differences (with respect to the reference electronic state at the value of R equal or close to that for which the potential energy is a minimum), for each atom, in the excited state of the complex.

Tables 4.1 to 4.3 do not show the densities on the hydrogen atoms because these do not participate, to any significant extent, in the Charge-Transfer stabilization of the organic complexes considered. This is to be expected because the H 1s atomic orbitals are quite tightly bound to the atoms (being part of the σ framework), and hence do not contribute to the delocalized π (or n) molecular donor orbitals.

The different fractional electron densities donated by the various atoms in the donor molecules can be explained in terms of the symmetries of the donor molecular orbital wavefunctions. (See Tables 4.1 to 4.5). For example, in the resting model 2, the benzene-oxygen singlet and triplet A_2 and A_1 states correspond to electronic transitions from the π $\psi(E_1a)$ and π $\psi(E_1b)$ benzene orbitals [61], respectively, to an antibonding $\pi^*(2p)$ molecular orbital of O_2. Hence the diametrically opposite carbon atoms C1 and C4 in the benzene ring act as the major donors in the stabilization of the A_2 state while the remaining carbon atoms (C2, C3, C5 and C6) play the major role in the stabilization of the A_1 state. This is to be expected since the nodal plane in the $\psi(E_1b)$ benzene orbital passes through C1 and C4 whereas the nodal plane in the $\psi(E_1a)$ wavefunction is perpendicular to this, resulting in the greatest electron density at atoms C1 and C4.

Similarly, in the resting model 1 the A_1 state corresponds to a donation from the $\psi(E_1a)$ benzene m.o. while the A_2 state corresponds to a transition from the $\psi(E_1b)$ orbital. This explains the electron density differences shown.

The axial model electron density differences and those for the other organic complexes are similarly explained.

Table 4.4 for the H_2O-O_2 complex shows that the states $^3A_2$ and $^3A_1$ in configurations M1 and M3 (See Figure 4.5) correspond to a transition from the nonbonding orbital on the O atom in H_2O to the antibonding π m.o. of O_2. In the $^3B_2$ state in configuration M3, the hydrogen atoms do play a small role in CT stabilization.

4.6 Conclusion

CNDO/S computations successfully reproduce the experimental behaviour of contact CT complexes. The calculated results are in agreement with experimental data wherever the latter are available. This implies that the calculated characteristics, such as binding energies and fractional electron density contributions, for which experimental results are not available are reasonably accurate also. More important, however, is the fact that CNDO/S computations provide a physical picture and account for the process of charge-transfer stabilization. This means that the method of computation can be used to theoretically predict the existence of charge-transfer spectra which have not been measured experimentally yet. In this way CNDO/S can serve as an excellent guide for future experimental work in the field.

In the next chapter it is shown how contact CT complexes can sustain population inversions resulting in a new class of lasers somewhat analogous to the commonly known diatomic rare gas-halide excimer lasers. CNDO/S calculations to guide experimental searches for such laser candidates then become important.

Before concluding, however, another important fact which makes CNDO/S a powerful tool must be pointed out. The mechanism which sustains a population inversion in a contact CT complex, to be described in the next chapter, does not rely on the fact that the excited state is charge-transfer stabilized. Similarly, CNDO/S, in no way, is restricted to molecular complexes which are charge-transfer stabilized. Hence, in principle, CNDO/S could be applied to molecular complexes which might have excited electronic states which are stabilized by means other than Charge-Transfer resonance. The number of molecular systems that can then be examined for potential as laser candidates, therefore, becomes even larger than the great number of Charge-Transfer systems known or suspected.

CHAPTER V

CONTACT CHARGE TRANSFER LASERS

5.1 Emission in Charge-Transfer Complexes

Absorption has been investigated experimentally in a wide range of charge-transfer complexes including contact CT complexes, [40-51, 53-58, 120]. However, fluorescence and phosphorescence measurements are not as plentiful. Furthermore, most of the luminescent (fluorescent and phosphorescent) measurements have been made at low temperatures, in many cases in solid state solutions [120]. Some fluorescent measurements have been made at room temperature [121], including those for 1,2,4,5-Tetra-cyanobenzene (TCNB-$C_{10}N_4H_2$) with various organic donors (TCNB consists of the benzene ring with four hydrogen atoms replaced by the -CN radical. 1,2,4,5 denote the positions, on the hexagonal benzene ring, of the -CN radical groups). The donors investigated included benzene, hexamethyl-benzene and mesitylene among others. Most phosphorescent measurements have been made at cryogenic temperatures [120].

Nagakura [120] explains the small oscillator strengths in emission in fluid CT complexes by the fact that once a CT complex has been formed (for instance by absorption of a photon), fast reorientation occurs such that the luminescent state is a high symmetry structure.

For example in the TCNB-hexamethylbenzene complex, the ground electronic state is a state of the lowest possible symmetry, the point group C_s. (See Appendix 3 for an outline of group theory.) This has been determined experimentally by Niimura *et.al.* [153]. Nagakura [120] has determined that the benzene rings of both the donor (hexamethylbenze or benzene) and the acceptor (TCNB) are aligned, in the equilibrium excited CT state configuration, leading to a relatively high symmetry, structure. In the notation of

Figure 5.1, the ground electronic state $E_N(R,Q_N)$ belongs to the point group C_s, whereas the fluorescent CT state, $E_v(R,Q_v)$, belongs to a higher symmetry point group. The intensity of the CT spectrum is governed by the transition moment through equations (A.51), (A.52), (A.62) and (2.76). Now in absorption, this transition moment is generally non zero. This follows from the character table for the point group C_s (See Appendix 3 and Cotton [61]). The C_s character table shows every transition would be allowed by either x,y, or z polarization. From the character tables of the higher point groups, it is seen that the percentage of transitions that would be allowed is much smaller decreasing with increasing symmetry. For example, in the point group C_{2v} if the direct product of the two relevant states belongs to the irreducible representation A_1, B_1, or B_2, electric dipole transitions would be allowed by z, x, or y polarization respectively. These three species constitute seventy five percent of the total number of irreducible representations here, the only dipole transition group theoretically forbidden being that for which the direct product of the two states belongs to the species A_2. In the point group C_{6v} only those transitions are dipole allowed for which the direct product belongs to the A_1 or E_1 irreducable representations. This constitutes only one third of the total number of species in this point group. As Nagakura [120] has shown, because of the higher symmetry of the fluorescent CT state of TCNB complexes with benzene and hexamethylbenzene the transition moment $<\overline{U}_{op}>$ (see equations (A.37), (A.51), (A.52), (A.62 and (2.76)) is relatively small.

At cryogenic temperatures, once CT absorption occurs, the complex does not have the flexibility to go into a higher symmetry structure. The emission transition probability is hence approximately equal to that in absorption. At higher temperatures in fluid media this is not the case, the luminescent state being of high symmetry and the transition moment is consequently small. This explains why fluorescence and phosphorescene measured at room temperature is substantially weaker than that at cryogenic temperatures.

It is important, however, to note that the contact CT complexes which have been considered in this work, and especially the pyrrole-oxygen complex which is, as shown below, the most important of the four complexes investigated as far as its potential as a laser candidate is concerned, are low symmetry structures. For instance, any non-planar pyrrole-oxygen complex configuration belongs to the lowest symmetry group C_s. This is mainly a consequence of the presence of the N atom in the pyrrole ring. Hence, in this case, group theoretical limitations on the emission transition probabilities such as those described above do not apply.

The molecular complex of aniline with oxygen also belongs to the point group C_s for any non-planar collision. Here also, the group theoretical restrictions on emission oscillator strengths do not apply.

In the case of the benzene-oxygen complexes the point groups are C_{2v} in the resting models and C_{6v} in the axial model. In the resting models the A_1 CT state is due to a $b_2 \rightarrow b_2$ transition and hence a fluorescent transition from this state to the ground state would be allowed with z polarization. The A_2 state is formed by a $b_1 \rightarrow b_2$ transition and hence a fluorescent transition here would be forbidden. This follows from the C_{2v} character table and the group-theoretical theorem mentioned in Appendix 3. Similar reasoning applied to the axial model shows that, once again fluorescence from the A_1 state would be allowed while that from the A_2 state would be forbidden.

One other phenomenon that plays an important role in the emission process is that of radiationless quenching. In fluid media this will obviously be more important than in solid matrices at cryogenic temperatures. This has been verified by experimental measurement [120]. Furthermore, this parasitic process is important for all complexes regardless of their symmetries. The effect of radiationless triplet quenching has been included in the rate equation analysis performed below, in Section 5.8, for the pyrrole-oxygen complex.

5.2 Population Inversion Mechanism in Contact CT Complexes

Contact CT complexes exhibit a unique means of sustaining an electronic population inversion.

The mechanism is illustrated in Figure 5.1. N and V denote the ground ("normal") and excited-CT states respectively, consistent with the notation due to Mulliken [51] and used in Chapter II. E_N and E_V are the energy levels of these states (sometimes also denoted by W_N and W_V). R is the collisional parameter (for instance, the distance between the donor and acceptor molecules - See also Figures 4.1 to 4.5 in Chapter IV). Q_N are all the other configuration coordinates, besides R, which minimize the energy of the complex in the ground electronic state. Q_V are the coordinates which minimize the energy in the excited state.

For the sake of argument, consider the irradiation, by a photon, of an organic-donor acceptor pair capable of forming a contact CT complex. The pair of molecules which is initially in the state $E_N(R, Q_N)$ absorbs this photon and undergoes a "vertical" transition forming the state $E_V(R, Q_N)$. Here, as a consequence of the Franck-Condon Principle [119], the internal coordinates Q_N do not change (The Franck-Condon Principle which states that the geometry of a molecule and its nuclear kinetic energy remain substantially unchanged during an electronic transition [130], and the Born-Oppenheimer Approximation which separates electronic and nuclear motions are both essentially the consequences of the great disparity between the masses of a

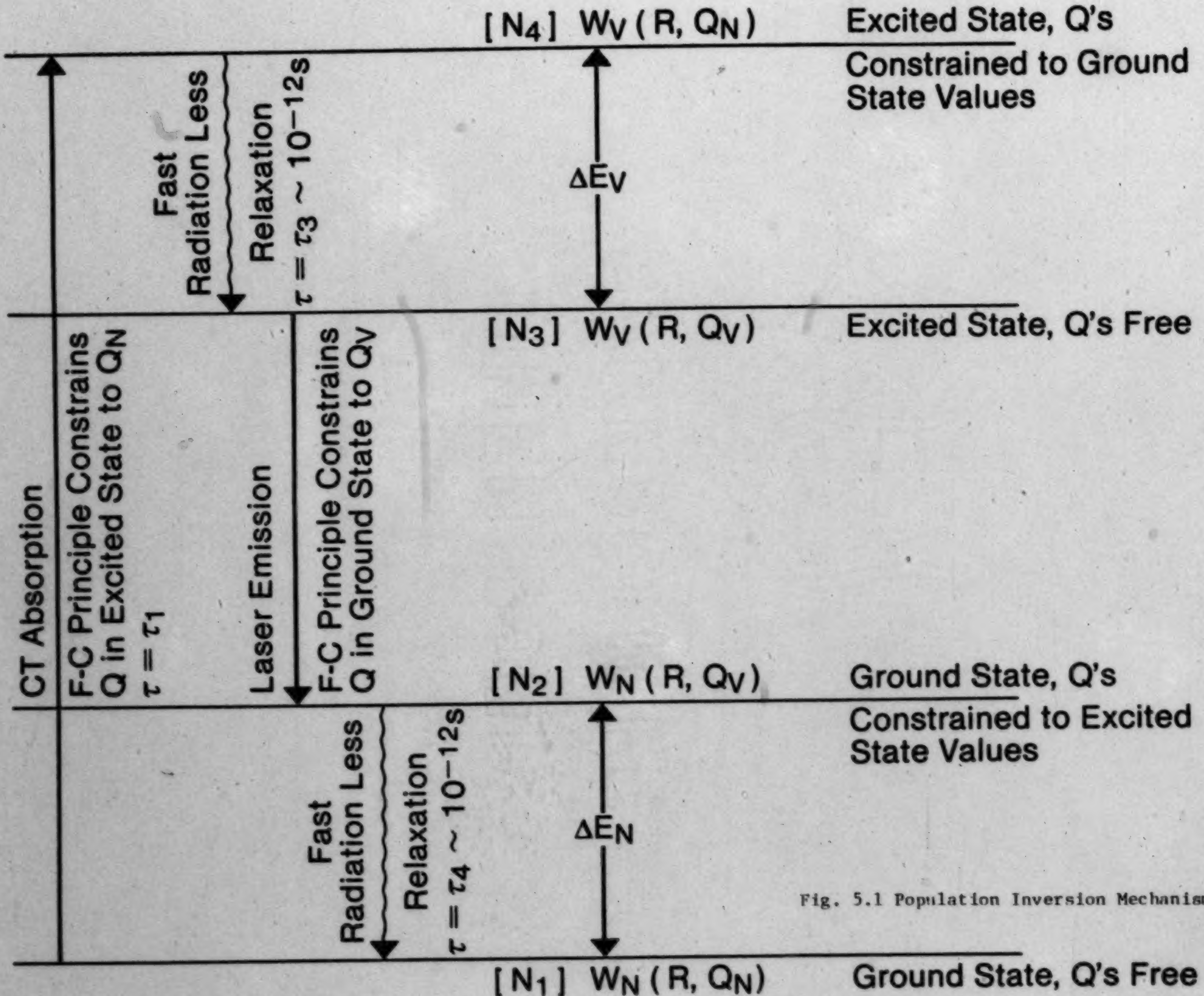

[N4] WV (R, QN)
Excited State, Q's
Constrained to Ground
State Values
Fast
Radiation Less
Relaxation
τ = τ3 ~ 10−12s
ΔEV
[N3] WV (R, QV)
Excited State, Q's Free
CT Absorption
F-C Principle Constrains
Q in Excited State to QN
τ = τ1
Laser Emission
F-C Principle Constrains
Q in Ground State to QV
[N2] WN (R, QV)
Ground State, Q's
Constrained to Excited
State Values
Fast
Radiation Less
Relaxation
τ = τ4 ~ 10−12s
ΔEN
[N1] WN (R, QN)
Ground State, Q's Free

Fig. 5.1 Population Inversion Mechanism

proton and an electron). Now fast radiationless relaxation, with characteristic times in the picosecond regime [57], take the complex to the state $E_V(R, Q_V)$ where the internal coordinates are free. (We assume here that the medium is fluid). Then, Franck-Condon radiative emission takes the complex to the ground electronic state $E_N(R, Q_V)$ in which the internal coordinates, Q, are constrained to the excited state values, Q_V. Finally, fast radiationless relaxation to the ground state $E_N(R,Q_N)$ occurs.

Both radiationless processes (which take the complex from $E_V(R,Q_N)$ to $E_V(R,Q_V)$ and from $E_N(R,Q_V)$ to $E_N(R,Q_N)$ are very fast processes compared to the radiative processes. In a typical organic CT complex the radiationless time constant is of the order of picoseconds. The radiative lifetimes are several orders of magnitude larger, being anywhere between nanoseconds and milliseconds [120]. (See also Appendix IV) and references [37], [154]).

The rate of depletion of $E_N(R,Q_V)$ by radiationless relaxation is fast compared to the emission from $E_V(R,Q_V)$. The emission process presents a "bottleneck", as it were, and a population inversion between $E_V(R,Q_V)$ and $E_N(R,Q_V)$ is established when the former state is populated.

The picture described above makes the important assumption that radiationless quenching of the upper laser state, $E_V(R,Q_V)$, is negligible. Such triplet quenching is discussed in detail below and it is shown that although this process limits gain, it does not eliminate it in a "typical" Contact CT Excimer Laser.

The simplified physical mechanism can be summarized by the following approximate equation

$$\frac{d[N_2]}{dt} = \frac{[N_3]}{\tau_2} - \frac{[N_2]}{\tau_4} \qquad (5.1)$$

where $[N_2]$, $[N_3]$ are the population densities (cm^{-3}) of the states $E_N(R,Q_V)$ and $E_V(R,Q_V)$ respectively, τ_2 and τ_4 are the lifetimes (radiative and radiationless associated with these two states.

Under steady state conditions

$$\frac{d[N_2]}{dt} = 0 \tag{5.2}$$

and

$$\frac{[N_3]}{[N_2]} = \frac{\tau_2}{\tau_4} \tag{5.3}$$

τ_4, the radiationless relaxation time constant, is of the order of picoseconds. τ_2 is an average radiative decay time which includes the effects of both spontaneous and stimulated emission. It is shown in Appendix IV that the spontaneous lifetime is typically about 1μs. For instance the spontaneous lifetime of the pyrrole-O_2 contact CT state is 0.6μs. The ratio $[N_3]/[N_2]$, which is a measure of the population inversion is then approximately 10^6. If the stimulated lifetimes are considered it follows that τ_2 will be larger and consequently the value 10^6, quoted above, is a lower limit of the inversion ratio.

In any practical system radiationless quenching of the laser state would decrease $[N_3]$ and increase $[N_2]$ reducing this ratio and consequently the gain also. In this case equation (5.1) is modified by the addition of a term like $k[N_3]$ on the right hand side which expresses the radiationless quenching of $E_V(R,Q_V)$ resulting in vibrationally excited ground state complexes, $E_N(R,Q_V)$.

5.3 Stokes Shift in Contact CT Complexes

Emission in a CT complex will be red shifted relative to absorption by an amount equal to $\Delta E_V + \Delta E_N$ (See Figure 5.1). This is the Stokes Shift and is analogous to the displacement between absorption and emission spectra between two bound electronic levels of stable molecules whose minima are displaced relative to each other. In stable molecules absorption normally occurs from the lowest vibrational level of the bound ground electronic state to an excited vibrational level of an upper electronic state. In the excited electronic state the molecules quickly relax to the corresponding lowest vibrational state from which emission occurs. The emission is consequently red-shifted relative to absorption.

The mechanism which causes the Stokes Shift in contact CT complexes is analogous. The difference here lies in the fact that the ground electronic state in these complexes is not bound as is the case for stable molecules.

For laser action to occur it is necessary that, besides the existence of a population inversion, there be no overlap between the emission and any absorption band.

Barring excited state absorption the Stokes Shift in contact CT complexes considered here is substantial enough to eliminate such an overlap.

A typical experimental value for this shift obtained for the CT complexes of TCNB is around 10,000 cm^{-1} in fluid media (at room temperature) [120].

In contact CT complexes this shift is expected to be even larger. This follows from the fact that the contrast between Q_N and Q_V is the larger for contact CT complexes than that for CT complexes which have bound ground electronic states [51]. In contact CT complexes Q_N corresponds approximately to the nuclear configuration of the free donor and acceptor molecules (although

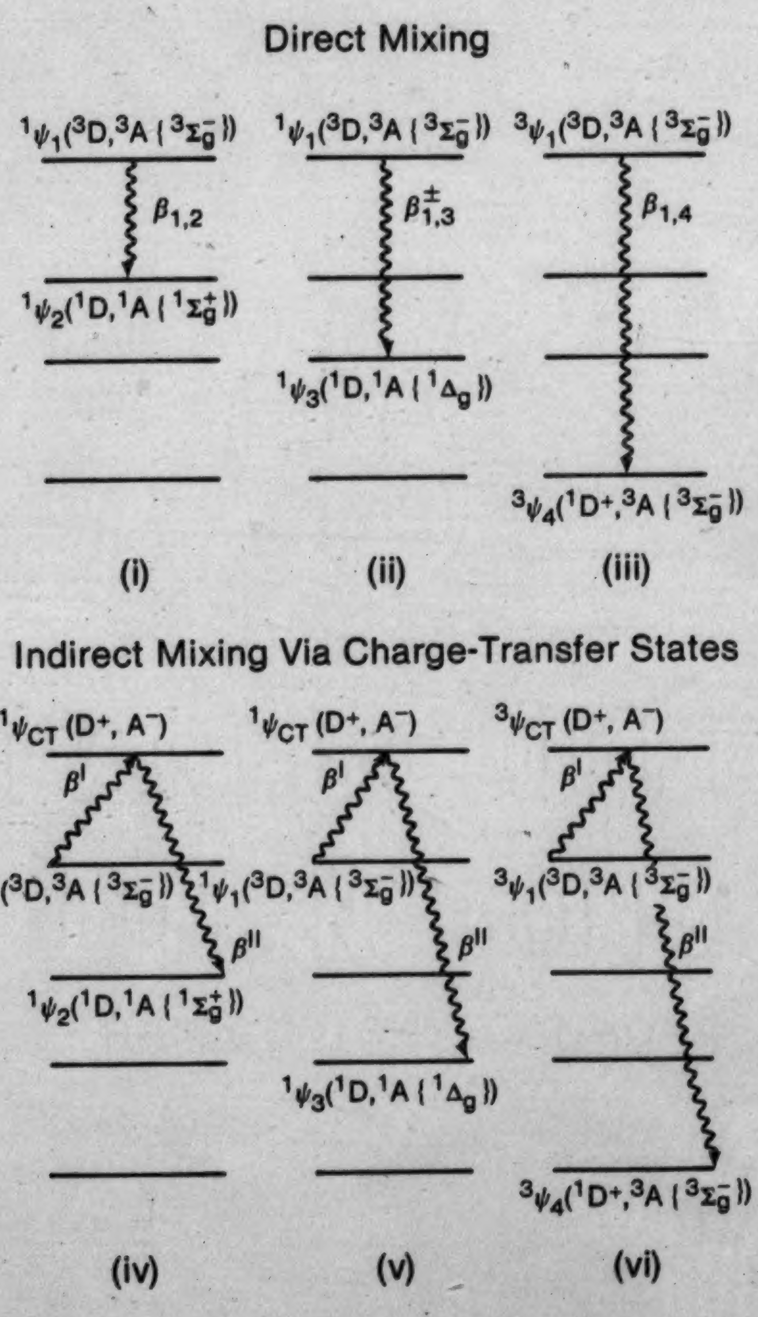

Direct Mixing
$^1\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
$\beta_{1,2}$
$^1\psi_2(^1D,^1A\{^1\Sigma_g^+\})$
$^1\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
$\beta^{\pm}_{1,3}$
$^1\psi_3(^1D,^1A\{^1\Delta_g\})$
$^3\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
$\beta_{1,4}$
$^3\psi_4(^1D^+,^3A\{^3\Sigma_g^-\})$
(i)
(ii)
(iii)
Indirect Mixing Via Charge-Transfer States
$^1\psi_{CT}(D^+, A^-)$
β^{I}
$^1\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
β^{II}
$^1\psi_2(^1D,^1A\{^1\Sigma_g^+\})$
$^1\psi_{CT}(D^+, A^-)$
β^{I}
$^1\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
β^{II}
$^1\psi_3(^1D,^1A\{^1\Delta_g\})$
$^3\psi_{CT}(D^+, A^-)$
β^{I}
$^3\psi_1(^3D,^3A\{^3\Sigma_g^-\})$
β^{II}
$^3\psi_4(^1D^+,^3A\{^3\Sigma_g^-\})$
(iv)
(v)
(vi)

Fig.5.2 A schematic representation of the coupling routes for electronic relaxation in the $[D....O_2]$ complex [177].

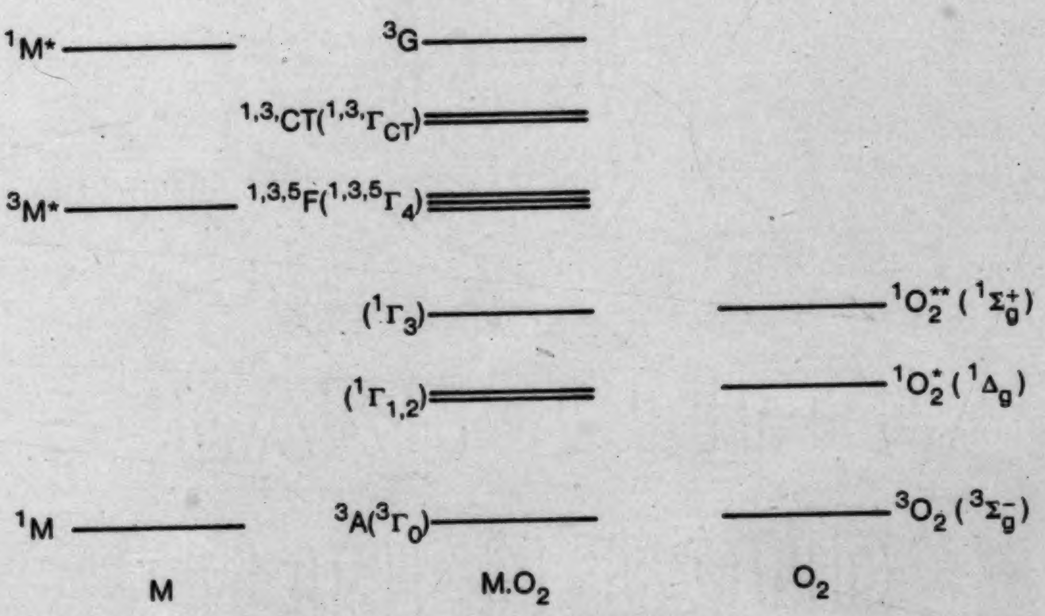
some orientations may be more favorable than others for CT absorption). On the other hand, Q_V corresponds to the equilibrium configuration for the pair of positive donor and negative acceptor ions [51].

5.4 Triplet Sensitized Pumping

In a specific contact CT laser the upper laser level density will depend very much on the method of pumping used. For instance, direct optical pumping of the state $E_N(R,Q_N)$ by absorption would not produce a substantial density in the state $E_V(R,Q_N)$ and hence in the upper laser state $E_V(R,Q_V)$ either. This follows from the fact that the optical absorption cross-section in the contact CT complexes considered here is small being of the order of 10^{-17} cm^2. This figure is obtained by using a decadic molar extinction coefficient of 100 (liters mole^{-1} cm^{-1}), which is a typical value for the complexes being considered. Mulliken and Tsubomura [49] have measured the experimental Σ values for various organic contact CT complexes and have also shown that these values can be explained in terms of intensity borrowing by the CT band from allowed donor $S_1 \rightarrow S_J (J \geq 2)$ transitions. The fraction of molecules in the upper state will also depend on the other quenching processes specific to the system being considered.

A more practical means of pumping would be to utilize the fact that, often, in organic molecules, the lowest triplet state T_1 is easily accessible by direct optical pumping of the singlet ground state to an excited singlet followed by efficient internal conversion (to the first excited singlet) and finally intersystem crossing to the triplet [161]. This mechanism can be very efficient and numerous examples are known where almost every photon incident on an organic molecule eventually leads to the production of the first triplet T_1 [7,161,171].

The method envisaged here requires the production of donor triplets by this mechanism with subsequent excitation of the triplet CT states of the



$^1M^*$
^3G
$^{1,3,}CT(^{1,3,}\Gamma_{CT})$
$^3M^*$
$^{1,3,5}F(^{1,3,5}\Gamma_4)$
$(^1\Gamma_3)$
$^1O_2^{**}\ (^1\Sigma_g^+)$
$(^1\Gamma_{1,2})$
$^1O_2^*\ (^1\Delta_g)$
^1M
$^3A(^3\Gamma_0)$
$^3O_2\ (^3\Sigma_g^-)$
M
$M.O_2$
O_2

Figure 5.3 Schematic diagram of the lower electronic energy levels of the $M.O_2$ complex between an aromatic donor molecule M and an oxygen molecule O_2 [155].

donor-acceptor complex by energy transfer. (See, for example, Figure 5.4). Triplet state energy exchange between various organic (energy) donors and (energy) acceptors (not to be confused by electron donors and electron acceptors) is a well documented process [161-170] both in rigid matrices and in fluid media. In the latter, energy transfer may occur on every collision between the energy donor and the energy acceptor [161] provided the transfer is exothermic.Endothermic transfer also occurs but the efficiency drops as endothermicity increases, as may be expected.

An important condition that must be satisfied if efficient triplet sensitized pumping is to be accomplished is, therefore, that the electron donor triplet be energetically higher than the CT triplet state of the electron donor acceptor complex.(See Figure 5.4).

In terms of the potential energy curves presented in Chapter IV, the *locally excited triplet state* curve (that is the interaction potential energy of the organic donor triplet T_1 with ground state O_2 as R is varied) should intersect the triplet CT curve.

CNDO/S computations (described in Chapter IV) were made for these locally excited triplet state curves for the complexes of benzene, aniline, and pyrrole with oxygen. It should be noted here that at large electron donor-electron acceptor distances, R, these potential energy curve values correspond to the calculated values of T_1 for the respective organic molecule.

The computed CNDO/S values obtained are given, and compared with the experimental values quoted in the literature, in Table 5.1.

From Table 5.1 and the results given in Chapter IV (Figures 4.1 to 4.3) it is seen that only in the case of the pyrrole-oxygen contact CT complex would triplet state exchange, discussed above, be exothermic. Hence, this is the only contact CT state which would yield to triplet sensitized pumping.

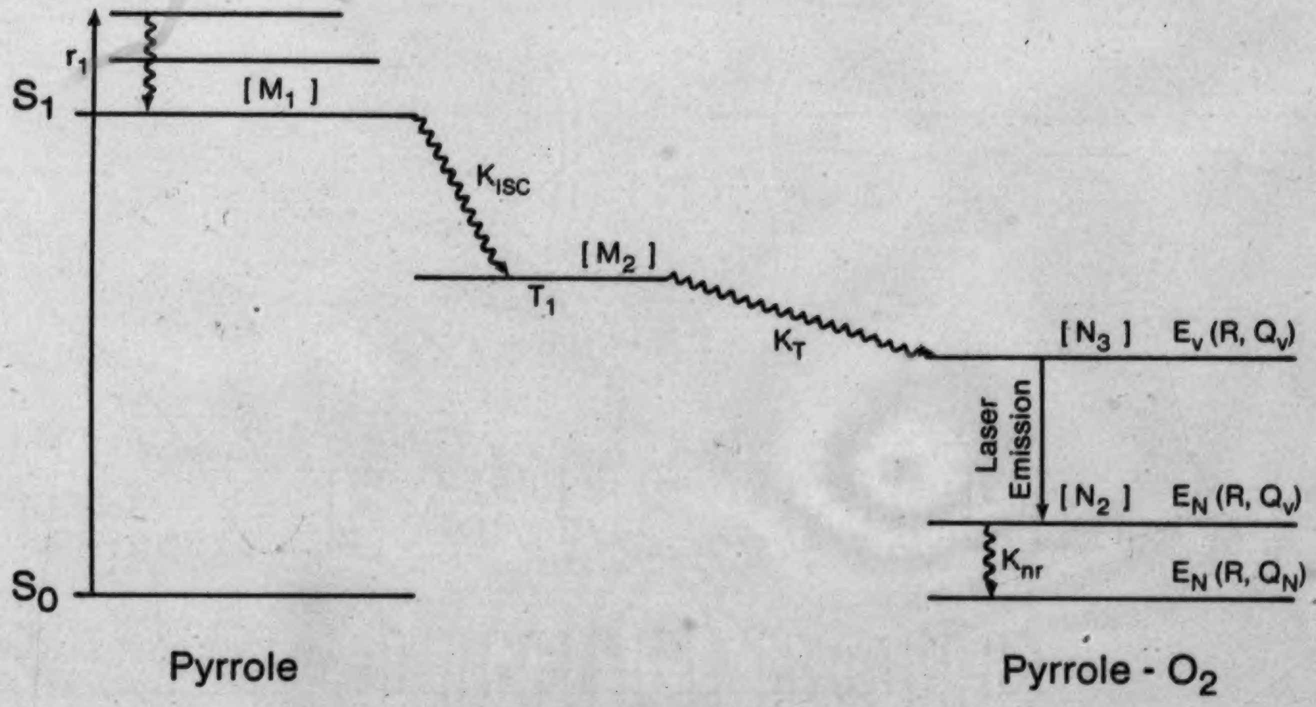

r_1
S_1
$[M_1]$
K_{ISC}
$[M_2]$
T_1
K_T
$[N_3]$
$E_v(R, Q_v)$
Laser Emission
$[N_2]$
$E_N(R, Q_v)$
K_{nr}
$E_N(R, Q_N)$
S_0
Pyrrole
Pyrrole - O_2

Fig.5.4 Triplet Sensitized Pumping

Table 5.1 Calculated and Experimental Values of T_1

Molecule	CNDO/S Value (ev)	Experimental Value (ev)
Benzene	3.43	3.65 [161]
Aniline	3.40	3.32 [129]
Pyrrole	3.99	4.4 [171]

Triplet sensitized pumping might be viewed from the point of view of curve crossing. If the locally excited triplet curve crosses with the triplet CT curve, then the latter would be populated by transfer of energy from the former. The condition that the potential energy curves cross automatically implies that triplet energy transfer must be exothermic, consistent with the discussion above. However, an additional criterion, which is not covered by the simple collisional picture, has to be satisfied. This is that the potential energy curve symmeteries be different. In that case [61]

$$< \Psi_{LE} | H | \Psi_{CT} > = o \qquad (5.4)$$

where Ψ_{LE} and Ψ_{CT} are the wavefunctions of the locally excited and CT states respectively. If Ψ_{LE}, and Ψ_{CT} belong to the same irreducible representation then the interaction energy integral above would in general be non-zero and the curves would tend to repel ("avoided curve crossing") [61,172-176].

In the pyrrole-oxygen complex the locally excited and CT states have different symmetries in the axial model and the Resting Model 1. In the

Resting Model 2 both the curves belong to the species A'.

The pyrrole-oxygen CT state can hence be pumped by transfer of electronic energy from the pyrrole triplet state. The rate equation analysis done below is for a pyrrole-oxygen Contact CT Excimer Laser pumped in this manner.

5.5 Radiationless Triplet Quenching

Parasitic triplet quenching by radiationless relaxation mechanisms would be detrimental to the production of gain by the pumping method described above in Section 5.5. Such triplet quenching would decrease gain by the following two ways:

1. Reduction of the organic molecule T_1 states *before* triplet energy exchange occurs,and
2. Reduction of the triplet CT states of the complex (the upper laser level) *after* triplet energy exchange.

Any rate equation treatment of the system must therefore take these effects into consideration. This is all the more so since the contact CT complexes investigated here involve O_2 as the acceptor. Molecular oxygen is known to be one of the most effective quenchers of organic triplets. For instance, the presence of even a trace of molecular oxygen may lead to erroneous results in experimental situations which do not call for the presence of any oxygen [177,178] by completely masking the behaviour of an organic triplet.

The quenching of the electron donor (for example pyrrole or benzene) triplet and that of the CT triplet will be treated separately below. It is expected that, although there may be other triplet quenching processes, quenching due to the presence of O_2 in the system will be the most important.

5.5.1 Rate of Radiationless Transitions

Before radiationless triplet quenching can be treated quantitatively it is necessary to extend the time dependent perturbation theory of Section

5.1 above in such a manner as to obtain the rate of radiationless transitions from any given state to a group of possible final states. The expression was first derived by Fermi [187] and is hence called Fermi's Golden Rule [17,64].

Consider a perturbation, analogous to that denoted by equation (A.40). The probability that this perturbation causes a transition from an initial state k to any final state q is then given by equation (A.51) reproduced below for convenience

$$P_{k\to q}(t) = \frac{|H^{(1)}_{kq}|^2}{h^2} \frac{\mathrm{Sin}^2[\frac{1}{2}(\omega_k-\omega_q-\omega)t]}{[\frac{1}{2}(\omega_k-\omega_q-\omega)]^2} \qquad (5.5)$$

Here we have considered a perturbation of the form

$$\mathcal{H}^{(1)}(\bar{r},t) = \mathcal{H}^{+}(\bar{r})\ e^{i\omega t} \qquad (5.6)$$

It is noted that here the perturbation operator $\mathcal{H}^{+}(\bar{r})$ is not exactly that expressed by (A.40) (which describes a dipole energy perturbation term important in radiative transitions). In (5.6) $\mathcal{H}^{+}(\bar{r})$ is an, as yet undefined, energy perturbation term which plays an important role in radiationless transitions. The derivation of (5.5) from (5.6) is analogous to that of (A.51) from (A.40). $P_{k\to q}(t)$ is a dimensionless transition probability. H_{kq} is an energy term (erg), t is the time (sec) that the perturbation lasts, ω_k, ω_q, ω are radian frequencies ($\sec^{-1}$) and h is the normalized Planck constant (erg sec). Let

$$\omega_k - \omega_q = \Delta\omega \qquad \left(\frac{1}{\sec}\right) \qquad (5.7)$$

$$\frac{1}{2}(\Delta\omega-\omega) = x \qquad \left(\frac{1}{\sec}\right) \qquad (5.8)$$

and

$$\rho_q(E) = \frac{dN_q}{dE} \qquad \left(\frac{1}{\text{erg}} \right) \tag{5.9}$$

where $\rho_q(E)$ is the density of final states in the region dE around $E_q = h\omega_q$ and dN_q is the (dimensionless) number of states in this range dE.

The probability of transition from a state k to a state q in the range E_q ± dE is then

$$P_{k\to q}(t)\ dN_q = P_{k\to q}(t)\ \rho_q(E)\ dE \tag{5.10}$$

The total probability of transition is therefore

$$P = {}_{-\infty}\int^{\infty} P_{k\to q}(t)\ \rho_q(E)\ dE \tag{5.11}$$

From (5.7) and (5.8)

$$hx = [(E_k - E_q) - E]/2 \tag{5.12}$$

Hence

$$dE = 2\ h\ dx \tag{5.13}$$

Therefore,

$$P = \frac{1}{h^2}\ {}_{-\infty}\int^{\infty} |H_{kq}^{(1)}|^2\ \frac{\text{Sin}^2(xt)}{x^2}\ \rho_q(E)\ dE \tag{5.14}$$

Defining a dimensionless quantity y as

$$y = xt, \quad \frac{dy}{dx} = t \tag{5.15}$$

yields

$$dE = \frac{2h}{t}\, dy \tag{5.16}$$

From (5.15), (5.16)and (5.14)

$$P = \frac{1}{2} \int_{-\infty}^{\infty} |H_{kq}^{(1)}|^2 \rho_q(E) \frac{\mathrm{Sin}^2(y)}{y^2}\; t \cdot 2h\, dy \tag{5.17}$$

$$P \simeq \frac{2|H_{kq}^{(1)}|^2}{h} \rho_q(E)\, t \int_{-\infty}^{\infty} \frac{\mathrm{Sin}^2 y}{y^2}\, dy \tag{5.18}$$

In deriving (5.18), $\rho_q(E)$ and $|H_{kq}^{(1)}|$ are assumed to be slowly varying (with respect to energy) quantities. This is a reasonable approximation since the integrand is a sharply peaked function centred around E_q [64]. Hence

$$P = \frac{2\pi t}{h} |H_{kq}^{(1)}|^2 \rho_q(E) \tag{5.19}$$

The transition rate from initial state k is then

$$R = \frac{dP}{dt} = \frac{2\pi}{h} |H_{kq}^{(1)}|^2 \rho_q(E) \qquad (\mathrm{sec}^{-1}) \tag{5.20}$$

This is Fermi's Golden Rule. This equation shows that the rate at which molecules in state k are deactivated is independent of time but proportional to the square of the magnitude of the perturbation matrix element and to the density of states which are coupled with the initial state k.

Equation (5.20) may be rewritten in a slightly modifed form

$$R = \frac{dP}{dt} = \frac{2\pi}{h} |H_{kq}^{(1)}|^2 \frac{\rho_q'(E)}{N(E)} \qquad (\mathrm{sec}^{-1}) \tag{5.21}$$

where by definition

$$\frac{\rho'_q(E)}{N(E)} = \rho_q(E) \qquad (\mathrm{erg}^{-1}) \qquad (5.22)$$

N(E) is the density of molecules in the final state in (cm^{-3}), $\rho'_q(E)$ is in ($\mathrm{cm}^{-3}\ \mathrm{erg}^{-1}$).

At present we are concerned only with radiationless transitions and therefore the final states, q, of importance here are those which are degenerate or nearly degenerate with the initial states k. In practice, the final states coupled to the initial state can be taken to be the vibronic manifold of the state E_q. The interaction energy term $H^{(1)}_{kq}$ due to the perturbation can hence be written more explicitly as a sum over these states.

$$R = (dP/dt) = (2\pi\rho'/hN) \sum_n |< \Psi^n_q | H^{(1)} | \Psi_k > |^2 \qquad (5.23)$$

where n runs over all the vibrational levels of the final state, E_q, to which radiationless transitions from the initial state, E_k, occur.

The derivation of equation (5.22) by use perturbation theory assumed that the total Hamiltonian, H, could be split into two parts, $H^{(0)}$ and $H^{(1)}$, (equation (A.3)). It was also assumed that $H^{(0)}$ gave rise to the stationary states which were described by a time independent wavefunction (equation (A.4)). This treatment is suitable when an external perturbation, such as an electromagnetic field, is present. It was shown above (Section 5.1) how this led to expressions for the radiative transition probabilities of stimulated emission and absorption. The application of equation (5.23) to radiationless transition, for example intersystem crossing within an isolated molecule, a process which is capable of occurring without the presence of an external perturbation, can be made be imaging $H^{(o)}$ to be zero. This implies that the radiationless transition is due to the total Hamiltonian of the isolated molecule itself. This is clearly in agreement with the experimental observation that, in general, radiationless transitions are intramolecular processes not requiring the presence of an external perturbing agent.

Equation (5.23) can hence be rewritten in a more general form which also describes the situation where a raditionless transition is triggered by an external influence as follows

$$R = (dP/dt) = (2\pi\rho'/hN) \sum_{n} |\langle\Psi_q^n|H|\Psi_k\rangle|^2 \qquad (5.24)$$

where

H is the total Hamiltonian of the system, and

n runs over all the vibrational levels of the final state, E_q, to which radiationless transitions from the initial state, E_k occur.

The total wavefunctions Ψ_q and Ψ_k are written, in the Born-Oppenheimer Approximation, as the product of electronic and nuclear wavefunctions $\Psi^{el}(\bar{r}_i, \bar{R}_k)$ and $\Psi^{nu}(\bar{R}_k)$ respectively (See equation (3.6) in Chapter III).

In equation (5.24), H is the total Hamiltonian of the system, which depends on both nuclear and electronic coordinates.

Furthermore, for the purposes of this work, the matrix element in equation (5.24) will be approximated [177, 188, 189] by writing it as the product of two components, one of which is an electronic term, and the other a nuclear term. The nuclear wavefunction term represents the overlap between the nuclear wavefunctions of the initial and final states. This term is usually called the Franck-Condon factor.

Hence

$$<\Psi_q^{n}|H|\Psi_k> = <\Psi_q^{el}\Psi_q^{nn}|H|\Psi_k^{el}\Psi_q^{nu}> \simeq <\Psi_q^{el}|H|\Psi_k^{el}>\cdot<\Psi_q^{nu}|\Psi_k^{nu}> \qquad (5.25)$$

Had H been a function of electronic coordinates only, this would be an exact equality. However, since H is a function of both electronic and nuclear coordinates, equation (5.25) is an approximation. This approximation, however, simplies the treatment considerably and will therefore be used here.

Equation (5.24) now becomes

$$(dP/dt)=(2\pi\rho'/hN)|<\Psi_q^{el}|H|\Psi_k^{el}>|^2\sum_n|<\Psi_q^{nu}|\Psi_k^{nu}>|^2 \qquad (5.26)$$

where the summation affects only nuclear wavefunctions, consistent with the approximation mentioned above.

The summation in equation (5.26) is the Franck-Condon factor defined as F_{kq}.

Hence

$$F_{kq} = \sum_n|<\Psi_q^{nu}|\Psi_k^{nu}>|^2 \qquad (5.27)$$

The other matrix element is, in the above approximation, an electronic factor β_{el} defined as

$$\beta_{el} = |\langle\Psi_q^{el}|H|\Psi_k^{el}\rangle| \qquad (5.28)$$

Hence (5.26) becomes, finally,

$$(dP/dt) = (2\pi\rho'/hN)\ \beta_{el}^2\ F_{kq} \qquad (5.29)$$

5.5.2 Electron Donor Radiationless Triplet Quenching by O_2

The quenching of organic triplets by molecular oxygen has been examined theoretically as well as experimentally [177-184]. Any rate equation analysis requires a numerical estimate for this process. Various estimates are available and these will be utilized in the rate equation analysis undertaken below.

/However, it is important to gain an insight to the physics of the process of donor triplet quenching by oxygen. Of particular relevance is the involvement of charge-transfer states in this process. It is necessary to find out if a CT complex is formed as an intermediate complex before the organic triplet is deactivated by a radiationless process. If, for example, every donor triplet which interacted with a ground state triplet oxygen molecule was radiationlessly deactivated by the formation of an intermediate CT complex triplet state, then the pumping mechanism described in Section 5.5 might not be successful, for then even after successful triplet energy exchange to the CT state the latter would have a relatively large probability of being dissociated radiationlessly.

There has been a lot of discussion in the literature regarding the actual physics of the triplet quenching mechanism [49,121-125,177-179,185]. The current view, supported by experimental evidence, [49,177], is that although charge-transfer interaction does play a large role in the quenching, a charge-transfer complex is *not* formed during radiationless deactivation of an organic triplet by molecular oxygen. The quenching occurs by an interaction of *virtual* CT states with the initial and final states of the quenching reaction [177]. The interaction forces are somewhat analogous to London dispersion forces. The latter forces, which have been used to explain van der Waal's forces, are due to the interaction of the ground electronic state (repulsive in the case of two helium atoms say) with all the excited states of the system. [The dispersion of light by a gas depends on the same quantities (the strengths of the transitions to all excited states) and hence the name "dispersion forces"][186]. In the same way that London dispersion forces between the ground repulsive state of two valence saturated atoms like He and the virtual excited electronic states of the system lead to an attractive force, the interaction of the initial system (comprising of an organic triplet and the ground state O_2 $^3\Sigma_g^-$, state) and final state (comprising of the quenching organic in its ground electronic state with or without vibrational excitation, and an oxygen molecule in the excited $^1\Sigma_g^+$ or $^1\Delta_g$ or the ground $^3\Sigma_g^-$ states) with virtual CT states gives a relatively high probability to the quenching process.

These ideas can be expounded quantitatively [177] by using Fermi's Golden Rule in the form of equation (5.29) derived above.

Consider an organic molecule, D, such as pyrrole, benzene or aniline in its first triplet state T_1 colliding with an oxygen molecule, A, in its ground electronic triplet state $^3\Sigma_g^-$. The total wavefunction describing this initial state will be denoted by $\Psi_1(^3D^3, A\{^3\Sigma_g^-\})$. The final states after quenching can be any of the following three systems:

(a) D in its ground singlet state and the oxygen molecule in its excited singlet state $^1\Sigma_g^+$. The total wavefunction describing this system can be written as $\Psi_2(^1D, {}^1A\{^1\Sigma_g^+\})$,

(b) D in its ground singlet state and oxygen in its excited singlet state ${}^1\Delta_g$, the total wavefunction being $\Psi_3({}^1D,\ {}^1A\{{}^1\Delta_g\})$,

(c) Both the organic molecule, D, and the oxygen molecule A in their ground electronic states with D being in a vibrationally excited state. The total wavefunction here can be written as $\Psi_4({}^1D^{\#},\ {}^3A\{{}^3\Sigma_g^-\})$, ${}^1D^{\#}$ representing the vibrationally excited organic molecule in its ground electronic state.

The schemes to be considered here involve quenching by direct interaction of the initial and final states and that due to the interaction of both the initial and final states with an intermediate CT state. This CT state can be a singlet or a triplet as shown in Chapter IV. These wavefunctions will be denoted by ${}^1\Psi_{CT}$ and ${}^3\Psi_{CT}$ (and correspond to ${}^1\Psi_v$ and ${}^3\Psi_v$ in the notation used in Chapter II). These interaction schemes are shown diagramatically in Figure 5.2 [177].

Equation (5.29) derived above is appropriate when the radiationless transitions occur as a result of direct mixing of the initial and final states [177,188]. Kawaoka *et.al.* [177] have derived an analogous expression, by use of second-order time dependent perturbation arguments, when indirect mixing the initial and final states occurs through an intermediate state. They show that in this case (5.26) modifies to

$$R = (dP/dt) = (2\pi\rho'/hN)\left|\langle\Psi_q^{el}|H|\Psi_{CT}^{el}\rangle\langle\Psi_{CT}^{el}|H|\Psi_k^{el}\rangle\right|^2$$

$$\sum_n\Big(\sum \frac{\langle\chi_q^n|\chi_{CT}^m\rangle\langle\chi_{CT}^m|\chi_i\rangle}{E_k - E_{CT}^m}\Big)^2 \qquad (5.30)$$

where the indices n and m run over the final and intermediate states q and CT respectively and where for convenience the nuclear wavefunctions Ψ^{nu}

are written as χ. Using

$$\sum_m |\chi^m_{CT}\rangle \langle\chi^m_{CT}| = 1 \tag{5.31}$$

it can be shown [177] that

$$R = (dP/dT) = (2\pi\rho'/hN)[|\langle\Psi^{el}_q|H|\Psi^{el}_{CT}\rangle \langle\Psi^{el}_{CT}|H|\Psi^{el}_k\rangle|^2/(E_k-E_{CT})^2_{el}]F_{kq} \tag{5.32}$$

where F_{kq} is the Franck-Condon factor defined by equation (5.27) and $(E_k-E_{CT})_{el}$ denotes the difference between the electronic energy levels of the initial state k and the intermediate CT state. Defining an electronic factor β'_{el} for this case as

$$\beta'_{el} = |\langle\Psi^{el}_q|H|\Psi^{el}_{CT}\rangle \langle\Psi^{el}_{CT}|H|\Psi^{el}_k\rangle/(E_k-E_{CT}| \tag{5.33}$$

equation (5.32) can be written as

$$(dP/dt) = (2\pi\rho'/hN)(\beta'_{el})^2 F_{kq} \tag{5.34}$$

which is exactly analogous to equation (5.29) for the case of direct mixing. β'_{el} in (5.34) plays the same role as β in (5.29).

From (5.29) and (5.34) the important quantities in determining the rate of radiationless relaxation are the matrix elements β and β', the Franck-Condon factors F_{kq} and the density of final states ρ'. In order to evaluate these terms, the wavefunctions of the initial, intermediate and final states have to be written.

The boundary condition on these wavefunctions is that the wavefunction of any state of D and A together (written as (DA)) reduce to the products of the separate molecule wavefunctions at infinite separation. Further, for mathematical convenience, it is required that wavefunctions corresponding to different (non stationary) states be orthogonal to one another at all intermolecular separations.

The wavefunctions are written as

$$\Psi_{(p,q)} = \mathcal{A} \ \Phi_D^p \, \Theta_A^q \tag{5.35}$$

where $\mathcal{A}$ is an antisymmetrizing operator which makes $\Psi_{(p,q)}$ antisymmetric with respect to permutation of any pair of electrons.

At infinite separation Φ_D^p and Θ_A^q satisfy the time independent Schroedinger wave equations

$$\mathcal{H}_D \, \Phi_D^p = E_D^p \, \Phi_D^p \tag{5.36}$$

$$\mathcal{H}_A \, \Theta_A^q = E_A^q \, \Theta_A^q \tag{5.37}$$

where $\mathcal{H}_D$ and $\mathcal{H}_A$ represent the isolated donor- and acceptor-molecule Hamiltonians respectively. The use of the product wavefunction (5.35) at finite molecular separations is a good approximation since the interactions being considered here are relatively weak.

It has been shown [177,190] that at infinite separation $\Psi_{(p,q)}$ is an eigenfunction of the total Hamiltonian of the system, $\mathcal{H}$. Hence

$$\mathcal{H} \, \Psi_{(p,q)} = (E_D^p + E_A^q) \, \Psi_{(p,q)} \tag{5.38}$$

Therefore, at infinite intermolecular separation, $\Psi_{(p,q)}$ represent the stationary states of the donor-acceptor system. At finite separations, however, the wavefunctions, $\Psi_{(p,q)}$, constructed in this manner are not exact eigenfunctions of H, and consequently, transitions between these non-stationary states may occur.

The total Hamiltonian of the system is written as

$$H = \left(-\frac{1}{2}\sum_{k_D} \nabla^2_{k_D} + \sum_{k_D<l_D} r^{-1}_{k_D l_D} - \sum_{k_D} \frac{Z_D}{r_{k_D D}}\right)$$

$$+ \left(-\frac{1}{2}\sum_{i_A} \nabla^2_{i_A} + \sum_{i_A<j_A} r^{-1}_{i_A} - \sum_{i_A} \frac{Z_A}{r_{i_A A}}\right)$$

$$- \sum_{i_A} \frac{Z_D}{r_{i_A D}} - \sum_{k_D} \frac{Z_A}{r_{k_D A}} + \sum_{k_D, i_A} r^{-1}_{i_A k_D} + \frac{Z_A Z_D}{R_{DA}} \qquad (5.39)$$

where the terms in the first bracket represent the Hamiltonian for the D molecule, those in the second bracket represent the Hamiltonian for the A molecule and the remaining terms are interaction terms. $Z_D/r_{i_A D}$ represents the interaction of electron i_A with all the nuclei of D and likewise for $Z_A/r_{k_D A}$. (All the nuclei in each molecule are "lumped together". Compare equations (3.1) to (3.10)). Spin-Orbit interaction is ignored in writing equation (5.39). To further simplify the calculations the following additional assumptions are made:

(1) The system is treated as a four electron system comprising of the two outermost parallel spin electrons of the organic molecule and the two outermost parallel spin electrons of the oxygen molecule. The rest of the electrons are considered together with the nuclei in D and A as comprising the cores of these two molecules. This approach is similar to that taken in

Chapter III in the formulation of the CNDO/S method.

(2) The molecular electronic orbital wavefunctions are written as antisymmetrized products of one-electron molecular orbitals. In order to orthogonalize the various $\Psi_{(p,q)}$, the molecular orbitals of D are orthogonalized with respect to those of A.

Kawaoka *et.al.* [177] consider the two cases of direct and indirect interation (equations (5.29) and (5.34) respectively). They have shown that the electronic matrix element

$$\beta_{el} \simeq 2\ \mathrm{cm}^{-1} \qquad \text{for direct interaction} \tag{5.40}$$

and

$$\beta'_{el} \simeq 20\ \mathrm{cm}^{-1} \qquad \text{for indirect interaction} \tag{5.41}$$

These values of β_{el} and β'_{el} are approximately independent of the final states of the system, (a), (b) or (c) above. In other words, for both the E→E process (in which the O_2 molecule ends up in an excited singlet state, with the organic triplet is quenched to its ground singlet state) and the E→V process (in which the organic triplet quenched to a vibrationally excited ground electronic state, the O_2 molecule staying in its ground electronic triplet state), the value of $\beta_{el} \simeq 2\ \mathrm{cm}^{-1}$ if the quenching occurs by direct interaction of the initial and final states and $\beta'_{el} \simeq 20\ \mathrm{cm}^{-1}$ if the quenching occurs via an intermediate virtual (unoccupied) CT state.

The four components of equations (5.29) and (5.34) can be written as

$$r_i = (2\pi\rho'/hN)\ (\beta_{el})^2_{i_{E-E}}\ (F_{kq})_{i_{E-E}} \tag{5.42}$$

$$r_{ii} = (2\pi\rho'/hN)\ (\beta'_{el})^2_{ii_{E-E}}\ (F_{kq})_{ii_{E-E}} \tag{5.43}$$

$$r_{iii} = (2\pi\rho'/hN)\ (\beta_{el})^2_{iii_{E-V}}\ (F_{kq})_{iii_{E-V}} \qquad (5.44)$$

$$r_{iv} = (2\pi\rho'/hN)\ (\beta'_{el})^2_{iv_{E-V}}\ (F_{kq})_{iv_{E-V}} \qquad (5.55)$$

(5.42) is the rate of radiationless quenching of the organic triplet by direct interaction of the initial and final states, k and q, with the final state q corresponding to cases (a) or (b) (O_2 in an excited singlet state).

(5.43) is the rate for the same process but via an interaction with an intermediate virtual (unoccupied) CT state.

(5.44) is the rate of radiationless quenching of the organic triplet by direct interaction of the initial and final states, k and q, for case (c) above (i.e. both the organic and O_2 molecues in their ground states with the organic molecule, D, vibrationally excited).

(5.45) is the rate for the same process but via an interaction with a virtual CT state.

Kawaoka *et.al.* [177] have shown that

$$(\beta_{el})_{i_{E-E}} \simeq (\beta_{el})_{iii_{E-V}} \simeq 2\ \text{cm}^{-1} \qquad (5.46)$$

$$(\beta'_{el})_{ii_{E-E}} \simeq (\beta'_{el})_{iv_{E-V}} \simeq 20\ \text{cm}^{-1} \qquad (5.47)$$

Defining

$$(2\pi\rho'/hN)\ (\beta_{el})^2_{i_{E-E}} \simeq (2\pi\rho'/hN)\ (\beta_{el})^2_{iii_{E-V}} = c \qquad (5.48)$$

and

$$(2\pi\rho'/hN)\ (\beta'_{el})^2_{ii_{E-E}} = (2\pi\rho'/hN)\ (\beta'_{el})^2_{iv_{E-V}} = c \qquad (5.49)$$

yields, from equations (5.42) to (5.45)

$$r_i = c(F_{kq})_{i_{E-E}} \qquad (5.50)$$

$$r_{ii} = c'(F_{kq})_{ii_{E-E}} \qquad (5.51)$$

$$r_{iii} = c(F_{kq})_{iii_{E-V}} \qquad (5.52)$$

$$r_{iv} = c'(F_{kq})_{iv_{E-V}} \qquad (5.53)$$

The total rate corresponding to the E-E process is therefore

$$r_{E-E} = r_i + r_{ii} = (c + c')\ (F_{kq})_{E-E} \qquad (5.54)$$

and the rate corresponding to the E-V process is

$$r_{E-V} = r_{iii} + r_{iv} = (c + c')\ (F_{kq})_{E-V} \qquad (5.55)$$

where we have used

$$(F_{kq})_{i_{E-E}} = (F_{kq})_{ii_{E-E}} = (F_{kq})_{E-E} \qquad (5.56)$$

and

$$(F_{kq})_{iii_{E-V}} = (F_{kq})_{iv_{E-V}} = (F_{kq})_{E-V} \qquad (5.57)$$

Equations (5.56) and (5.57) imply that the Franck-Condon factors are approximately the same for both the direct mixing and indirect mixing E-E processes. Similarly they are approximately the same for both the direct mixing and indirect mixing E-V processes. These are reasonable approximations because the Franck-Condon factor is related to the amount of energy converted to vibrational energy, ΔE cm^{-1}, by the following relation [177,191-193]

$$F \approx 0.15 \times 10^{-[(\Delta E-4000)/5000]} \qquad (5.58)$$

From equations (5.54) and (5.55) it can be seen that the relative rates of quenching by the E-E and E-V processes depend mainly on the Franck Condon factors. For an E-E process the amount of electronic energy, ΔE, converted to vibrational energy is smaller than for the E-V process. In other words

$$\Delta E_{E-E} < \Delta E_{E-V} \qquad (5.59)$$

Consequently, from (5.58)

$$F_{E-E} > F_{E-V} \qquad (5.60)$$

Kawaoka *et.al.* [177] have shown that, in general, F_{E-E} is between 100 and 1000 times larger than F_{E-V}, and that $c' \approx 10c$.

5.5.3 Radiationless Quenching of Triplet CT State

The spontaneous emission lifetime of the triplet CT state is expected to be approximately 1μs (See Appendix IV). The lifetime of the radiationless decay of this state is not known accurately. However, from the discussion of triplet quenching in subsection 5.6.2 above, an estimate for this time may be made.

Since molecular oxygen is known to be one of the most efficient triplet quenchers [177,178], it will be assumed here that the major loss in the upper laser state occurs by collisions with O_2.

As mentioned in subsection 5.6.2, the radiationless quenching of an organic triplet can occur by direct mixing or by indirect mixing of the initial and final states. Furthermore, the quenching may be described as either an E→V or an E→E process. The relevant rates for these four components of the process are given by equations (5.43) to (5.45). As explained above, quenching by indirect mixing via an intermediate CT state is approximately ten times faster than by direct mixing.

Indirect mixing of the type that occurs in the quenching of D by O_2 is unlikely here simply because the existence of an intermediate CT state is not likely here. Such a CT state would have to be a state of the complex $D-O_2-O_2$.

Under identical circumstances then, radiationless quenching of the laser state is expected to be approximately an order of magnitude slower than quenching of the electron donor triplet by O_2.

In the "worst case" radiationless quenching of the triplet CT state may be taken to be as efficient as that of the electron donor triplet by O_2.

5.6 Summary of Effects Due to the Presence of O_2 [155]

It will be useful to summarize the various effects due to the interaction of O_2 with organic molecules and to bring out the common features involved in all of them.

The oxygen molecule has a triplet ground state ($^3\Sigma_g^-$) and has excited singlet states ($^1\Delta_g$, $^1\Sigma_g^+$) with excitation energies of 7882 cm^{-1} and 13,121 cm^{-1}

respectively.

The interaction of ground state oxygen with an aromatic molecule leads to the following photophysical observations:

i) contact CT spectra [40-57]

ii) enhanced S_o-T_1 absorption in the aromatic [49, 121-125]

iii) aromatic triplet ($T_1 \equiv {}^3M^*$)quenching [177-180]

iv) energy transfer from aromatic triplet to O_2 yielding singlet excited state O_2 [177-180]

v) oxidation of aromatic [182]

All these processes have some common characteristics which will now be discussed.

In Figure 5.3, the states of the isolated aromatic molecule, M, the isolated O_2 molecule and the states of the system $M \cdot O_2$ are shown.

The $M \cdot O_2$ states originate as follows (the notation used is that of Tsubomura and Mulliken [49], with that of Kearns *et.al.* [177,194] shown in parentheses)

$^3A(^3\Gamma_o)$, from $^1M, ^3\Sigma_g^-$

$(^1\Gamma_{1,2})$, from ^1M, $^1\Delta_g$

$(^1\Gamma_3)$, from ^1M, $^1\Sigma_g^+$

$^{1,3,5}F(^{1,3,5}\Gamma_4)$, from $^3M^*$, $^3\Sigma_g^-$

$^{1,3}CT(^{1,3}\Gamma_{CT})$, from $^2M^+$, $^2O_2^-$

and

^3G, from $^1M^*$, $^3\Sigma_g^-$

Here ^1M, $^3M^*$ and $^1M^*$ are the ground singlet and the first excited triplet and singlet states (S_o, T_1 and S_1) of M. $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$ are the ground triplet and the first two excited singlet states of O_2.

5.6.1 Contact CT Spectra

As mentioned in Chapter II, Murrell [58,74,75] and Tsubomura and Mulliken [49] have shown that contact CT spectra, corresponding to the spin-allowed transition ^3A- ^3CT in Figure 5.3, derive their intensity from the ^3G- ^3A transition. The ^3G- ^3A transition in turn derives its intensity from the ^1M- $^1M^*$ (S_o - S_1) transition of the aromatic. When the S_o-S_1 transition is forbidden, as in benzene, the CT transition borrows its intensity from a higher excited singlet state of M via a higher excited triplet state of the $M{\cdot}O_2$ system. Tsubomura and Mulliken have shown that decadic molar extinction coefficients thus calculated agree well with experimentally measured values.

5.6.2 Enhanced S_o-T_1 Spectra

It has been shown experimentally that the intensity of S_o-T_1 spectra of aromatic molecules is enhanced substantially by the presence of O_2 [49,121-125]. This transition, spin-forbidden in the isolated aromatic, corresponds to the spin-allowed ^3A-^3F transition in the $M{\cdot}O_2$ system. Murrell [58,74,75] and Tsubomura and Mulliken [49] have shown that this transition gains intensity by interaction of the ^3F and ^3CT states. As mentioned above the ^3A-^3CT transition obtains its intensity by interaction of the ^3CT state with the ^3G state. The ^3A-^3G transition derives its intensity in turn from the ^1M-$^1M^*$ (S_o-S_1) transition. Hence, the contact CT spectra and S_o-T_1 enhanced spectra both ultimately derive their intensity from the organic ^1M-$^1M^*$ transitions.

Hoijtink's [185] proposal that the ^3A-^3F transition gains its intensity by direct interaction between the ^3F and ^3G states does not appear to be accurate. Such a direct interaction mechanism leads to smaller calculated electronic matrix element, β_{el}, (see equation (5.28) above) than necessary to explain the experimentally observed values of the enhanced intensity. Indirect mixing via the ^3CT state accounts properly for the experimentally observed values (via the matrix element β'_{el} (see equation (5. 33) above) [177].

5.6.3 Aromatic Triplet Quenching by O_2

The initial state here corresponds to $\Psi_1(^3D, {}^3A\{^3\Sigma_g^-\})$ in the notation of Kawaoka *et.al.* [177]. (See also subsection 5.6.2 above). This is the state F of the $M \cdot O_2$ system in Figure 5.3. The final states ((a), (b) and (c) in subsection 5.6.2) correspond to the states $(^1\Gamma_3)$, $(^1\Gamma_{1,2})$ and $^3A^{\#}(^3\Gamma_o{}^{\#})$ where the last state is vibrationally excited. As explained in subsection 5.6.2, the formation of electronic excited oxygen (final states $^1\Gamma_{1,2}$ and $^1\Gamma_3$) occurs between 100-1000 times faster than formation of vibrationally excited ground electronic state of M (corresponding to $^3A^{\#}$). Further Kawaoka *et.al.* [177] have shown that these processes occur by interaction with the CT states, $^{1,3}CT$, at a rate approximately ten times faster than if the process occurred by direct interaction of the initial and final states.

It may be said therefore that all the three processes mentioned, namely contact CT absorption (and emission), enhanced S_o-T_1 absorption and aromatic triplet quenching involve interaction of the CT states and the rates of these processes are, in the final analysis, governed by the rate of the transition (radiative or radiationless) S_1-S_0 of the aromatic.

6

5.6.4 Production of Excited Singlet O_2 and Oxidation of Aromatic

Production of excited singlet O_2 is a direct consequence of the quenching of the aromatic triplet explained above. Obviously, the presence of excited O_2 in the system generally enhances the rate of oxidation reactions. For example, Kautsky [195] studied the photo-oxidation of spatially isolated sensitized and acceptor molecules, and found that at a low optimum oxygen pressure it was possible to selectively excite a sensitizer and produce oxidation of a distant acceptor molecule. Kautsky concluded that this long-range transfer of energy was due to the diffusion of excited (singlet) O_2 molecules (which have long radiative lifetimes), produced by quenching of the triplet state sensitizer. It has been shown, further, that singlet state molecular oxygen produced in the reaction of sodium hypochlorite with hydrogen peroxide [196], or in an rf discharge [197], reacts with various organic compounds to give products which are identical to those produced in photosensitized oxidation of these compounds [198,199].

5.7 Rate Equation Analysis

The pumping mechanism described in Section 5.5 is illustrated in Figure 5.4 which shows the energy levels of the isolated aromatic and those of the CT complex.

Of the systems investigated here the one most suited for this type of pumping is the pyrrole-oxygen complex because, as mentioned previously, the ^{3}CT state in this case is lower than the T_1 state of pyrrole.

The important steps in this pumping process are the following

(1) Optical pumping of the pyrrole S_1 state. This is an allowed transition and the S_1 state may be populated directly by $S_0 \rightarrow S_1$ transitions and by $S_0 \rightarrow S_J$ transitions ($J \geq 2$) with subsequent radiationless internal conversion to S_1. This rate of pumping is denoted by r_1(cm^{-3} sec^{-1}).

(2) Intersystem crossing from the S_1 to the T_1 states. The rate constant for this process is denoted by $K_{ISC}(\sec^{-1})$.

(3) Triplet-Triplet energy exchange between the pyrrole T_1 state and the ^{3}CT state. The rate constant for this process is denoted by $K_T(\sec^{-1})$.

(4) Laser emission between the ^{3}CT state and the level $E_N(R,Q_V)$ (See Figure 5.1). The radiative decay time here is denoted by $K_R(\sec^{-1})$.

(5) Radiationless Relaxation of the state $E_N(R,Q_V)$ to $E_N(R,Q_N)$ (See Figure 5.1).

The ^{3}CT state shown in Figure 5.4 is the $E_V(R,Q_V)$ state (the upper laser level) in Figure 5.1. This is equivalent to the assumption that the triplet-triplet exchange process characteristic time is long enough to allow the internal coordinates Q to take on values which minimize E_V. The densities (cm^{-3}) of the various states are denoted by $[M_1]$, $[M_2]$, $[N_3]$, $[N_2]$ and $[N_1]$. See Figure 5.4 and Figure 5.1. For each of the states a rate equation may be written. Hence,

$$\frac{d[M_1]}{dt} = r_1 - K_F[M_1] - K_{ISC}[M_1] \qquad (5.61)$$

where, in general, K_F is the fluorescence decay time constant ($\sec^{-1}$) of S_1 and the other quantities have been defined above.

$$\frac{d[M_2]}{dt} = K_{ISC}[M_1] - K_T[M_2] - K_{Tq}[M_2] - K_{TT}[M_2]^2 \qquad (5.62)$$

where, $K_{Tq}(\sec^{-1})$ is the rate at which T_1 is quenched radiationlessly by O_2 and K_{TT} (cm^{3}sec^{-1}) is the rate of self quenching of T_1.

$$\frac{d[N_3]}{dt} = K_T[M_2] - K'_{Tq}[N_3] - K'_{TT}[N_3]^2 - K_R[N_3] \qquad (5.63)$$

where K'_{Tq} (sec^{-1}) is the rate at which ^3CT is quenched by collisions with O_2, K'_{TT} ($cm^3\ sec^{-1}$) is the self quenching rate and K_R (sec^{-1}) is the radiative decay time constant of the ^3CT state.

$$\frac{d[N_2]}{dt} = K_R[N_3] - K_{nr}[N_2] \qquad (5.64)$$

where K_{nr} (sec^{-1}) is the rate of radiationless relaxation of the state $E_N(R,Q_V)$ to $E_N(R,Q_N)$. Equation (5. 64) is identical to (5. 1) with

$$K_R = \tau_2^{-1} \text{ and } K_{nr} = \tau_4^{-1} .$$

To simplify the analysis steady-state conditions will be assumed. The left-hand sides of equations (5.61) to (5.64) are hence all zero.

It should be noted here that the quantitative analysis, based on equations (5.61) to (5.64), presented below can only by a very approximate one since many of the above rate constants are not known accurately at present. The sample calculation presented assumes an experimental test cell, 10 cm in length, 5 cm in diameter, filled with 10 torr of pyrrole and 10 torr of O_2.

The rate of optical pumping of S_1 can be written as [7]

$$r_1 = \frac{\Sigma MI}{h\nu}\ (cm^{-3}\ sec^{-1}) \qquad (5.65)$$

where Σ is the decadic molar extinction coefficient (liters $cm^{-1} mole^{-1}$), M is the molar concentration (moles $litre^{-1}$), I is the incident radiative power per cm^2 (Watts cm^{-2}), h is Planck's constant (Joule.sec) and ν the frequency of absorbed photon (Hz).

For pyrrole [171] the peak absorption occurs at 48,190 cm^{-1} and Σ_{max} = 7590 (liters $cm^{-1} mole^{-1}$). Assuming an incident (optical pumping) power of 25 KW cm^{-2}, this leads to a value of

$$r_1 = 1.2 \times 10^{23} \text{ cm}^{-3} \text{ sec}^{-1} \tag{5.66}$$

Now in pyrrole it can be assumed that practically every molecule in the S_1 state eventually results in one in the T_1 state [171]. This is the reason given by Hovrath and Kiss [171] for their failure to observe fluorescence in pyrrole.

Hence in equation (5.61) $K_F \simeq 0$. This leads to

$$[M_1] = r_1/K_{1SC} \tag{5.67}$$

An experimental value for K_{1SC} is unavailable. However, for benzene this value is approximately 10^7 sec^{-1} [161]. Making the reasonable assumption that the value of K_{1SC} in pyrrole is comparable yields the steady state value

$$[M_1] = 10^{16} \text{ cm}^{-3} \tag{5.68}$$

The value of the rate constant, K_T, for triplet energy exchange is unknown also. This is the most difficult value to estimate. In other small molecular systems involving potential energy crossing this rate constant lies between 10^{-9} and 10^{-11} cm^3 $molecule^{-1}$ sec^{-1} [200]. Assuming a value of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} as a "typical" value yields

$$K_T = 4 \times 10^7 \ \text{sec}^{-1} \tag{5.69}$$

at the pressures under consideration.

The value of K_{Tq}, the rate at which pyrrole triplets are quenched by O_2 is taken to be approximately the same as the experimental rate quoted by Snelling [180] for benzene. This experimental value is 5×10^{-11} cm^3 molecule^{-1} sec^{-1}. This leads to

$$K_{Tq} = 2 \times 10^7 \ \text{sec}^{-1} \tag{5.70}$$

where, as in obtaining the value for K_T, the density of quencher molecules is estimated from the stipulated conditions of pressure. Ignoring self quenching equation (5. 62) leads to a steady state value

$$[M_2] \approx \frac{1}{6} \times 10^{16} \ \text{cm}^{-3} \tag{5.71}$$

In order to obtain the density of states, $[N_3]$, in the upper laser level it is necessary to know the rate constants in equation (5.63) . K'_{Tq} is the rate of radiationless decay of the upper laser state by collisions with O_2. It would be reasonable to assume a value of K'_{Tq} to be approximately equal to that of K_{Tq}, the rate of quenching of pyrrole triplets by O_2. This corresponds to "worst case" conditions (See subsection 5.6.3 above). Hence

$$K'_{Tq} \approx K_{Tq} \approx 2 \times 10^7 \ \text{sec}^{-1} \tag{5.72}$$

The radiative decay time constant is taken to be the spontaneous emission rate (10^6 sec^{-1}. See Appendix IV). This can be done since if the spontaneous and stimulated emission lifetimes are τ_{sp} and τ_{st} respectively, and the total radiative lifetime is τ_R, then

$$\frac{1}{K_R} = \tau_R = \tau_{sp} + \tau_{st} = \frac{1}{K_{sp}} + \frac{1}{K_{st}} \qquad (5.73)$$

From (A.24)

$$K_{st} \equiv R_{q\to k} = B_{qk}\,\rho \qquad (5.74)$$

and

$$A_{kq} \equiv K_{sp} \qquad (5.75)$$

Using (A.70) and (A.66) shows that the spontaneous emission rate is the limiting rate process here, since then

$$K_{st} = B_{qk}\,\rho = \frac{A_{kq}}{e^{h\nu/KT}-1} \qquad (5.76)$$

where hν in the pyrrole-O_2 complex is approximately 2.8 ev. Using this value in (5.76) shows that

$$K_{st} << K_{sp} \qquad (5.77)$$

Ignoring self quenching in (5.63) this finally leads to

$$[N_3] = 3 \times 10^{15}\ \text{cm}^{-3} \qquad (5.78)$$

If an emission cross-section of 10^{-17} cm^2 (See Appendix IV) is assumed consistent with measurements of extinction coefficients of approximately 100 in absorption, this value yields an upper value for gain, g,

$$g \underset{\sim}{<} 0.03 \text{ cm}^{-1}$$

The neglect of self quenching(rate constants K_{TT} and K_{TT}' in equations (5.62) and (5.63) is not a bad approximation. For instance, with self quenching ignored the densities of the relevant triplets $[M_2]$ and $[N_3]$ were obtained to be approximately 10^{15} cm^{-3} and 3×10^{15} cm^{-3} . Now a reasonable value rate for the self quenching process is [129]

$$K_{TT} = 10^{10} \text{ mole}^{-1} \text{ sec}^{-1} \qquad (5.79)$$

Then $K_{TT}[M_2] = 2 \times 10^4 \text{ sec}^{-1}$ (5.80)

and $K_{TT}[N_3] = 2 \times 10^5 \text{ sec}^{-1}$ (5.81)

In comparison with the other rate constants in equation (5.62) and (5.63) these values are orders of magnitude smaller. Hence the estimates for $[M_2]$ and $[N_3]$ obtained by ignoring self quenching are approximately correct. Generally, the effect of triplet quenching of an organic by collision with the ground state singlet is smaller than self quenching of the triplet [129]. Hence the estimate for gain obtained above is reasonable.

CHAPTER VI

CONCLUSION AND OUTLOOK

The theoretical basis for the existence of a new class of lasers analogous to the well-known diatomic excimer lasers has been established. The "Contact Charge Transfer Excimer Lasers"utilize the extra degrees of nuclear freedom that exist in polyatomic complexes of two valence saturated molecules.

The CNDO/S method describes the behaviour of the excited electronic states and can be used to investigate the potential of numerous other complexes as laser molecules.

There are several obstacles that have to be overcome before a contact CT Excimer Laser can be operated in the laboratory. These are briefly discussed below together with suggestions on future work that may prove fruitful.

It is expected that one of the major problems that will have to be overcome in practice will be the prevention of irreversible chemistry. The contact CT complexes investigated above involve the oxygen molecule in an acceptor role. The latter is a reactive molecule and hence experimental conditions would have to be strictly regulated if the pumping mechanism suggested is to work. For example, it would be necessary to keep the incident radiation frequency below the threshold for photochemical reactions in the mixture irradiated. Initial experiments could be conducted with a monochromatic but tunable light source (such as a tunable dye laser).

For molecular systems involving O_2, the production of the excited singlet states of the latter during radiationless quenching of organic triplets could present another problem. The enhancement of irreversible chemistry by the presence of singlet O_2 would have to be studied carefully in experimental situations.

Another problem related to irreversible photochemistry is that of predissociation [73]. If in any atomic (or molecular) system certain discrete energy levels a,b,c,... of a series of states A have the same energy as a continuous range M of energy levels of a series of states B the former assume, to a certain degree, properties of the latter. Normally, the continuous range M corresponds to the system "flying apart" with various amounts of kinetic energy [73]. Hence once the system is in any of the states a,b,c,... it will, after some time, enter the range M and break up. Such radiationless decomposition is called the *Auger process.* If the continuous levels M correspond to dissociation, the process is called *predissociation;* when it corresponds to ionization it is called *preionization* or *autoionization* [73, 186].

A major route of predissociation is the excitation of the system by absorption of light which takes the molecule to levels energetic enough for photochemical decomposition by predissociation to occur. In the pumping mechanism proposed in Chapter V, therefore, predissociation may cause parasitic loss of the laser state. In order to minimize any such effects it would be necessary to control the energy of the incident photons.

Further work, both theoretical and experimental regarding other contact CT pairs would be useful. For example, it would be instructive to find whether other acceptors, less reactive than molecular O_2 form contact CT complexes. Molecules like CO_2 which are known to act as acceptors could be investigated. Similarly, other donors could be investigated.

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APPENDIX I

INTERACTION OF RADIATION WITH MATTER

This appendix outlines some well known results, in particular it treats radiative emission and absorption. We start by outlining time dependent perturbation theory in which the total Hamiltonian is treated as a sum of two parts, one of which is time independent and for which stationary states wavefunctions exist. The second part of Hamiltonian incorporates the time dependence expressions for radiative transition probabilities are hence derived. The semi-classical thermodynamic treatment for spontaneous emission, formulated originally by Einstein is also presented.

The interaction of radiation with matter gives rise to three important phenomena namely *stimulated emission*,*(stimulated) absorption* and *spontaneous emission*. These processes can be accounted for by quantizing both the radiation and the atom or molecule with which the field interacts [17,142]. Such an approach requires the elegant but somewhat formidable formalism of quantum electrodynamics [143]. For this reason, in the present work, a semiclassical approach will be used in which the atomic or molecular system is treated quantum mechanically, but the electromagnetic radiation is formulated classically.

The semiclassical approach has the drawback of not accounting for spontaneous emission in a natural way. However, this phenomenon can be studied somewhat indirectly by including Einstein's thermodynamic treatment (in the form of the Einstein A and B coefficients). This is the approach taken here. Time-dependent perturbation theory will be used in which the electromagnetic field is included as a small time-dependent perturbation of the Hamiltonian of the isolated atomic or molecular system.

A.1.1 Time-dependent Perturbation Theory [17]

Since the electromagnetic radiation, taken here as a classical harmonic field, is time dependent, the total Hamiltonian of the system will also be time-dependent. Hence the time-independent Schroedinger equations (2.11) and (3.1) cannot be used. This simplification of the Schroedinger equation, used in Chapter II, is only applicable to cases where the potential energy term in the Hamiltonian is not a function of time, in which case the total wavefunction can be separated in space and time as follows

$$\Psi(\bar{r},t) = \exp\{-i(E/\hbar)t\}\Psi_E(\bar{r}) \qquad (A.1)$$

where $\bar{r}$ denotes the spatial dependence of a wavefunction (on both the nuclear and electronic spatial coordinates, $\bar{r}_i$ and $\bar{R}_k$ of Chapters II and III), E is the energy of the system and h the normalized Planck constant.

In the case of a time-dependent potential energy term in the Hamiltonian, it is necessary to start from the fundamental time-dependent Schroedinger equation

$$H\Psi(\bar{r},t) = ih \frac{\partial}{\partial t} \Psi(\bar{r},t) \qquad (A.2)$$

from which the time-independent forms given in (2.11) and (3.1) can be derived by using the wave equation represented by (A-1) [64].

In time-dependent perturbation theory the full Hamiltonian, H, of the system (comprising of radiation and matter) is split up into two parts

$$H(\bar{r},t) = H^{(o)}(\bar{r}) + H^{(1)}(\bar{r},t) \qquad (A.2)$$

where the zeroth-order Hamiltonian, $H^{(o)}(\bar{r})$, is time-independent and all time dependence is included in the perturbation Hamiltonian $H^{(1)}(\bar{r},t)$.

Since $H^{(o)}(\bar{r})$ is independent of t, there do exist stationary-state (time-independent) wave functions for the zeroth-order Hamiltonian, $H^{(o)}(\bar{r})$. Hence a time-independent equation can be written for this part of the full Hamiltonian

$$H^{(o)}(\bar{r})\,\psi_{E_n}(\bar{r}) = E_n\psi_{E_n}(\bar{r}) \tag{A.4}$$

where $\psi_E(\bar{r})$ is an eigenfunction of the zeroth-order Hamiltonian $H^{(o)}(\bar{r})$ corresponding to the eigenvalue E_n. It should be noted here that stationary states do not exist for the full Hamiltonian $H(\bar{r},t)$, since the latter is a function of time. Once time dependence is introduced via the perturbation Hamiltonian, one can no longer talk about eigenfunctions and eigenvalues.

In effect equation (A.4) ignores the presence of the electromagnetic field and this must therefore be included in the perturbation Hamiltonian $H^{(1)}(\bar{r},t)$.

Time dependent perturbation theory now assumes an expansion for the total wavefunction in terms of a complete set of zero-order wavefunctions $\psi_{E_n}(\bar{r})$ of equation (A.4). In order to do that it is necessary to introduce the time dependence of $\Psi(\bar{r},t)$ in the expansion coefficients. Hence, the following expansion is used

$$\Psi(\bar{r},t) = \sum_{j=1}^{\infty} a_j(t)\,\psi_j(\bar{r})\,\exp\{-i(E_j/h)t\} \tag{A.5}$$

where j represents a set of quantum numbers which uniquely identify a state of the unperturbed system. The nonstationary character of the total wavefunction, $\Psi(\bar{r},t)$, is reflected in this expansion. The state described by $\Psi(\bar{r},t)$ is assumed to be a mixture of stationary states of the unperturbed

Hamiltonian (atom or molecule in the absence of the field) with the coupling coefficients, $a_j(t)$, depending on time.

Substituting the expansion (A.5) into (A.2) yields

$$[H^{(o)}(\bar{r}) + H^{(1)}(\bar{r},t)] \sum_{j=1}^{\infty} a_j(t)e^{-i\omega_j t} \psi_j(\bar{r}) = ih \frac{\partial}{\partial t} \sum_{j=1}^{\infty} a_j(t)\, e^{-i\omega_j t} \psi_j(t) \tag{A.6}$$

where the angular frequency, ω_j, is defined by

$$\omega_j = \frac{E_j}{h} \tag{A.7}$$

which follows from

$$h\nu_j = \frac{h\omega_j}{2\pi} = h\omega_j = E_j \tag{A.8}$$

Now since the set $\{\psi_j(\bar{r})\}$ forms stationary state eigenfunctions of the unperturbed Hamiltonian it must also satisfy the time dependent Schroedinger equation from which the time independent form is derived by use of equation (A.1). Hence

$$H^{(o)}(\bar{r})\psi_j(\bar{r})\, e^{-i\omega_j t} = ih \frac{\partial}{\partial t}\, \psi_j(\bar{r})\, e^{-i\omega_j t} \tag{A.9}$$

Therefore

$$H^{(o)}(\bar{r}) \sum_{j=1}^{\infty} a_j(t)e^{-i\omega_j t} \psi_j(\bar{r}) = ih \sum_{j=1}^{\infty} a_j(t) \frac{\partial}{\partial t} \psi_j(\bar{r})e^{-i\omega_j (t)} \tag{A.10}$$

Expanding (A.6), using (A.10) multiplying throughout by $\psi_q^*(\bar{r})e^{i\omega_q t}$ and integrating over all spatial coordinates yields

$$\frac{d}{dt}a_q(t) = \frac{1}{i\hbar}\sum_{j=1}^{\infty} a_j(t)e^{-i(\omega_j-\omega_q)t} H_{qj}^{(1)}(t) \quad (q=1,2\ldots\infty) \tag{A.11}$$

where

$$H_{qj}^{(1)}(t) = \int\psi_q^*(\bar{r})\mathcal{H}^{(1)}(\bar{r},t)\psi_j(\bar{r})d\bar{r} \equiv \langle\psi_q(\bar{r})|\mathcal{H}^{(1)}(\bar{r},t)|\psi_j(r)\rangle \tag{A.12}$$

(the Dirac brackets in (A.12) denote integration over spatial coordinates only).

There are an infinite number of equations in set (A.11). one for each value of $q=1,2,\ldots\infty$. In order to solve this infinite set of coupled, first-order differential equations (A.11) is integrated over time from 0 to t yielding

$$a_q(t) = -\frac{i}{\hbar}\sum_{j=1}^{\infty}\{\int_0^t a_j(t)e^{-i(\omega_j-\omega_q)t}H_{qj}^{(1)}(t)dt\} + c_q,\ q=1,2,\ldots\infty \tag{A.13}$$

where c_q is a constant of integration which is determined by the initial conditions of the problem under consideration.

It is apparent that to solve for the qth coefficient, $a_q(t)$, we must know all the coefficients, including $a_q(t)$, since they appear on the right-hand side of (A.13). Hence solution of (A.13) is not possible without approximating.

It will be assumed here that the perturbation Hamiltonian, $\mathcal{H}^{(1)}(\bar{r},t)$, is small. From (A.11), then, the rate of change of each coefficient, $a_q(t)$, can also reasonably be assumed to be small.

Let the system initially (i.e. at t=o) be in the kth quantum state. Let a small perturbation be introduced at this time, t=o. A short time later (time = t), none of the coefficients will have changed significantly, so $a_k(t) \simeq 1$ will be the largest, and the superposition of stationary states making up the total wavefunction $\Psi(\overline{r},t)$ (given by (A.5) will be dominated by the kth state. In the zeroth-order approximation, which in effect ignores the perturbation, is therefore

$$a_j(t) \simeq \delta_{jk} \text{ for small } t>o \tag{A.12a}$$

and

$$\Psi(\overline{r},t) \simeq \psi_k(\overline{r})\, e^{-i(E_k/h)t} \quad \text{for small } t>o \tag{A.12b}$$

Substituting (A.13a) into (A.13) yields

$$a_q(t) \simeq -\frac{i}{h}\sum_{j=1}^{\infty}\{{}_o\int^t \delta_{jk}\, e^{-i(\omega_j-\omega_q)t}\, H^{(1)}_{qj}(t)dt\} + c_q$$

$$a_q(t) \simeq -\frac{i}{h}\,{}_o\int^t e^{-i(\omega_k-\omega_q)t}\, H^{(1)}_{qk}(t)dt + C_q$$

Now for $q \neq k$, $a_q(o) = o$ since the system is initially in the kth state. Further, the perturbation matrix element $H^{(1)}_{qk}(o)$ is also zero since the perturbation is "switched on" at t=o. Hence $c_q = o$ and

$$a_q(t) \simeq -\frac{i}{h}\,{}_o\int^t e^{-i(\omega_k-\omega_q)t}\, H^{(1)}_{qk}(t)\, dt \quad q \neq k \tag{A.13c}$$

For q=k, $a_q(o) = a_k(o) = 1$. Hence $c_q = 1$. Therefore

$$a_q(t) = a_k(t) = 1 - \frac{i}{h} \int_0^t e^{-i(\omega_k - \omega_q)t} H_{kk}^{(1)}(t)dt \quad q=k \qquad (A.13d)$$

Equations (A.13c) and (A.13d) are first-order time dependent perturbation theory coefficients. The corresponding first-order wavefunction can be obtained by evaluating the coefficients $a_j(t)$ using these equations and then substituting in the expansion given by (A.5).

The physical interpretation of the coefficients $a_j(t)$ in (A.5) can be obtained by realizing that the probability of finding the system in state q at time t_1 (when initially it was in state k before the perturbation was applied) is given by

$$P_{k\to q}(t_1) = \left|\int \psi_q^*(\bar{r}) e^{i(E_q/h)t_1} \Psi(\bar{r},t_1) d\bar{r}\right|^2 \qquad (A.14)$$

Now using the fact that the eigenfunctions $\psi_q(\bar{r})$ are orthornormalized and substituting (A.5) into (A.14) immediately yields

$$P_{k\to q}(t_1) = |a_q(t_1)|^2 \qquad (A.14)$$

Equation (A.13c) is therefore an important result since it yields the probability of a transition from state k to state q as a result of a time-dependent perturbation.

A.1.2 The Electromagnetic Radiation Field

As mentioned before the interaction of radiation with matter will be treated by considering a classical electromagnetic field as a perturbation. The approach will be to first write down the perturbation Hamiltonian $H^{(1)}(\bar{r},t)$ due to the radiation field and then use time dependent perturbation theory, outlined above, to expand $\Psi(\bar{r},t)$, the total wavefunction, in the stationary states of the unperturbed system. The expansion coefficients thus obtained represent the transition probabilities caused by the presence of the electromagnetic field. The radiation field will be taken to be that of a classical plane wave. Furthermore, in the following treatment, only the effects due to the electric component of the electromagnetic field will be considered, the effects of the magnetic component being neglected. This is normally justified since the electric field effects are significantly larger than those of the magnetic field.

The treatment in this section will therefore lead to an expression for the electric dipole transition moment. The corresponding quadrupole and magnetic dipole moments are orders of magnitude smaller and although these are very important in many practical situations (especially in not allowing any transition to be rigorously *forbidden*) they will, nonetheless, be ignored here, for simplicity.

The elctric component of a plane monochromatic electromagnetic wave, at any point (x,y,z), is given by

$$\overline{E}(\overline{R},t) = E_x(\overline{R},t)\overline{a}_x + E_y(\overline{R},t)\overline{a}_y + E_z(\overline{R},t)\overline{a}_z \qquad \text{(A.16)}$$

where $\overline{R}$ is the distance from the source, $\overline{a}_x$, $\overline{a}_y$ and $\overline{a}_z$ are unit vectors in the x, y and z directions respectively. Each component will be given by an equation like the following

$$E_x(\overline{R},t) = E_x^{\circ}\, e^{i\overline{K}\cdot\overline{R}}\, e^{i\omega t} + E_x^{\circ}\, e^{-i\overline{K}\cdot\overline{R}}\, e^{-i\omega t} \qquad \text{(A.17)}$$

where the plane wave propagates in the direction of $\overline{K}$ which is perpendicular to both $\overline{E}$ and $\overline{B}$ (the magnetic field component) [144,145].

Consider the situation where the molecular system has a dipole moment given by (2.71) which is repeated here for convenience

$$\overline{U}_{op} = e \sum_k z_k \overline{R}_k - e \sum_i r_i \tag{A.18}$$

Then the perturbation Hamiltonian is given by the interaction of this dipole with the field. In the far field this can be written as

$$H^{(1)}(\overline{r},t) = \overline{U}_{op} \cdot \overline{E}(\overline{R},t) \tag{A.19}$$

The full Hamiltonian then becomes

$$H(\overline{r},t) = H^{(o)}(\overline{r},t) + \overline{U}_{op}\overline{E}(\overline{R},t) \tag{A.20}$$

$H^{(o)}$ is the unperturbed Hamiltonian of the molecular system (that is the Hamiltonian which expresses the stationary states of the system) This time independent part will have stationary states described by (A.4).

Writing the dipole moment in terms of its components

$$\overline{U}_{op} = U_x \overline{a}_x + U_y \overline{a}_y + U_z \overline{a}_z \tag{A.21}$$

and using (A.16) in (A.19) yields

$$H^{(1)}(\overline{r},t) = [U_x E_x(\overline{R},t) + U_y E_y(\overline{R},t) + U_z E_z(\overline{R},t)] \tag{A.22}$$

If the molecular system is initially in state k then the relevant matrix elements to be evaluated are $H^{(1)}_{kk}$ and $H^{(1)}_{kq}(t)$. From (A.22) it can be seen that each matrix element will consist of three terms, an x term, a y term and a z term. Consider the x term alone

$$H^{(1)}_{kqx} = <\psi_q(\bar{r})|H^{(1)}_x(\bar{r},t)|\psi_k(\bar{r})> \qquad (A.23)$$

$$H^{(1)}_{kqx} = <\psi_q(\bar{r})|U_x E_x(\bar{R},t)|\psi_k(\bar{r})> \qquad (A.24)$$

Using (A.17) this yields

$$H^{(1)}_{kqx} = <\psi_q(\bar{r})|U_x E^o_x e^{i\bar{K}\cdot\bar{R}} e^{i\omega t} + U_x E^o_x e^{-i\bar{K}\cdot\bar{R}} e^{-i\omega t}|\psi_k(\bar{r})> \qquad (A.25)$$

It should be recalled here that the integration in these equations, (A.23) to (A.25) is over spatial coordinates only.

The y and z terms are similar.

In order to evaluate (A.25) a further simplification will be made. It can be shown [17] that if the wavelength of the incident radiation is large compared to the dimensions of the atom or molecule perturbed by it, then taking

$$e^{i\bar{K}\cdot\bar{R}} = e^{i\bar{K}\cdot\bar{R}_o} = \text{constant} \qquad (A.26)$$

is a reasonable approximation.

Using (A.26) in (A.25) yields

$$H^{(1)}_{kqx} = E^o_x[e^{i\bar{K}\cdot\bar{R}_o} e^{i\omega t} <\psi_q(\bar{r})|U_x|\psi_k(\bar{r})> + e^{-i\bar{K}\cdot\bar{R}_o} e^{-i\omega t} <\psi_q(\bar{r})|U_x|\psi_k(\bar{r})>] \qquad (A.27)$$

Similarly

$$H^{(1)}_{kqy}=E^{o}_{y}[e^{i\bar{K}\cdot\bar{R}_{o}}e^{i\omega t}<\psi_{q}(\bar{r})|U_{y}|\psi_{k}(\bar{r})>+e^{-i\bar{K}\cdot\bar{R}_{o}}e^{-i\omega t}<\psi_{q}(\bar{r})|U_{y}|\psi_{k}(\bar{r})>] \qquad (A.28)$$

and

$$H^{(1)}_{kqz}=E^{o}_{z}[e^{i\bar{K}\cdot\bar{R}_{o}}e^{i\omega t}<\psi_{q}(\bar{r})|U_{z}|\psi_{k}(\bar{r})>+e^{-i\bar{K}\cdot\bar{R}_{o}}e^{i\omega t}<\psi_{q}(\bar{r})|U_{z}|\psi_{k}(\bar{r})>] \qquad (A.29)$$

Defining

$$< U_{kqx} > = < \psi_{q}(\bar{r})|U_{x}|\psi_{k}(\bar{r}) > \qquad (A.30)$$

$$< U_{kqy} > = < \psi_{q}(\bar{r})|U_{y}|\psi_{k}(\bar{r}) > \qquad (A.31)$$

and

$$< U_{kqz} > = < \psi_{q}(\bar{r})|U_{z}|\psi_{k}(\bar{r})> \qquad (A.32)$$

The total matrix perturbation Hamiltonian matrix element is

$$H^{(1)}_{kq}(t) = H^{(1)}_{kqx}(t) + H^{(1)}_{kqy}(t) + H^{(1)}_{kqz}(t) \qquad (A.33)$$

Using equations (A.27) to (A.32) in (A.33) yields

$$H^{(1)}_{kq}(t) = [e^{i\bar{K}\cdot\bar{R}_{o}}e^{i\omega t} + e^{-i\bar{K}\cdot\bar{R}_{o}}e^{-i\omega t}][E^{o}_{x}<U_{kqx}> + E^{o}_{y}<U_{kqy}> + E^{o}_{z}<U_{kqz}>] \qquad (A.34)$$

Defining

$$\overline{E}^{+} = e^{i\overline{K}\cdot\overline{R}_o}[E_x^o \overline{a}_x + E_y^o \overline{a}_y + E_z^o \overline{a}_z] \qquad (A.35)$$

and

$$\overline{E}^{-} = e^{-i\overline{K}\cdot\overline{R}_o}[E_x^o \overline{a}_x + E_y^o \overline{a}_y + E_z^o \overline{a}_z] \qquad (A.36)$$

and recognizing that, from (A.21) and (A.30) to (A.32)

$$< \overline{U}_{op} > = < \psi_q(\overline{r}) | \overline{U}_{op} | \psi_k(\overline{r}) > = < U_{kqx} > \overline{a}_x + < U_{kqy} > \overline{a}_y$$
$$+ < U_{kqz} > \overline{a}_z \qquad (A.37)$$

yields finally

$$H^{(1)}_{kq}(t) = < U_{op} > \cdot [\overline{E}^{+} e^{i\omega t} + \overline{E}^{-} e^{-i\omega t}] \qquad (A.38)$$

$H^{(1)}_{kk}(t)$ is similarly derived.

These matrix elements then enable one to calculate radiative transition probabilities by the time-dependent perturbation relationships derived in Section

For convenience let the perturbation Hamiltonian be separated into spatial and harmonic temporal parts

$$H^{(1)}(\overline{r},t) = H^{+}(\overline{r})\, e^{i\omega t} + H^{-}(\overline{r})\, e^{-i\omega t} \qquad (A.39)$$

where

$$H^{+}(\overline{r}) = \overline{U}_{op} \cdot \overline{E}^{+} \qquad (A.40)$$

and

$$H^{-}(\bar{r}) = \bar{U}_{op} \cdot \bar{E}^{-} \qquad \text{(A.41)}$$

and where $\bar{E}^{+}$ and $\bar{E}^{-}$ are defined by (A.35) and (A.36). Note that equation (A.39) follows immediately from equation (A.22) if the definitions given by equations (A.16), (A.17), (A.21), (A.35), (A.36), (A.40) and (A.41) are used.

A.1.3. Radiative Transition Probabilities

It is now possible to derive expressions for the probabilities with which the molecular system under consideration will undergo radiative transitions. Since these transitions occur because of the perturbation caused by the presence of an external electromagnetic field the phenomena are properly described as *stimulated* absorption and *stimulated* emission. However, the adjective stimulated is normally not used for absorption since this process cannot occur spontaneously unlike emission, which can [148].

As mentioned previously, the semiclassical approach taken here does not naturally account for the phenomenon of spontaneous absorption, unless thermodynamic constraints are placed.

As before let the molecular system be in the quantum mechanical state k before the perturbation is experienced. Let this perturbation be due to the presence of a harmonic electromagnetic field such that the perturbation Hamiltonian is given by (A.39). Then as shown above the probability that a transition to the state q occurs is given by $|a_q(t)|^2$ of equation (A.13c).

Substituting (A.39) into (A.13c) yields

$$a_q(t) = -\frac{i}{h} \int_0^t e^{-i(\omega_k-\omega_q)t} \langle \psi_q(\bar{r}) | H^{+}(\bar{r}) e^{i\omega t}$$

$$+ H^{-}(\bar{r}) e^{-i\omega t} | \psi_k(\bar{r}) \rangle \, dt \qquad \text{(A.42)}$$

Hence

$$a_q(t) = -\frac{i}{h} \int_o^t \{H^+_{kq}\, e^{-i(\omega_k-\omega_q-\omega)t} + H^-_{kq}\, e^{-i(\omega_k-\omega_q+\omega)t}\}\, dt \tag{A.43}$$

where

$$H^+_{kq} = < \psi_q(\bar{r})|\mathcal{H}^+(\bar{r})|\psi_k(\bar{r})> \tag{A.44}$$

and

$$H^-_{kq} = <\psi_q(\bar{r})|\mathcal{H}^-(\bar{r})|\psi_k(\bar{r})> \tag{A.45}$$

Once again, the integrations in (A.44) and (A.45) are over coordinate space only. Hence in (A.43) the matrix elements H^+_{kq} and H^-_{kq} can be removed from under the integral sign. Doing this and evaluating the definite integral in equation (A.43) results in

$$a_q(t) = -\frac{i}{h} H^+_{kq} \left[\frac{e^{-i(\omega_k-\omega_q-\omega)t}}{-i(\omega_k-\omega_q-\omega)} \right]_o^t - \frac{i}{h} H^-_{kq} \left[\frac{e^{-i(\omega_k-\omega_q+\omega)t}}{-i(\omega_k-\omega_q+\omega)} \right]_o^t$$

Hence

$$a_q(t) = \frac{H^+_{kq}}{(E_k-E_q-h\omega)} [e^{-i(\omega_k-\omega_q-\omega)t} - 1] + \frac{H^-_{kq}}{(E_k-E_q+h\omega)} [e^{-i(\omega_k-\omega_q+\omega)t} -1] \tag{A.46}$$

where equation (A.7) has been used. The square of the amplitude of this term gives the probability that the molecular system will undergo a transition from the initial state k to any other state q in the presence of a monochromatic electromagnetic field with an angular frequency ω. Equation (A.46) gives an interesting result since it shows that the transition probabilities attain their maximum values when the incident radiation has a quantum energy which is equal to the energy difference between two states E_k and E_q, that is when

$$h\nu = h\omega = E_k - E_q \tag{A.47}$$

Here E_k can be higher or lower than E_q. If $E_k > E_q$ then the transition probability calculated is that of *stimulated emission*. For the case when $E_k < E_q$, the transition probability corresponds to that of *absorption*.

The fact that $a_q(t)$ takes on maximum values when (A.47) holds is easily proved by applying L'Hospital's Rule [146] to (A.46).

For the purposes of this work, only the case when the electromagnetic field photon energy, $h\omega$, is nearly resonant with the energy spacing $E_k - E_q$ will be considered.

For resonant stimulated emission ($h\omega \approx E_k - E_q$ and $E_k > E_q$) the first term in (A.46) dominates. Hence the probability of stimulated emission is then

$$|a_q(t)|^2 \approx \frac{|H^+_{kq}|^2}{h^2(\omega_k-\omega_q-\omega)^2} \left|\mathrm{Cos}(\omega_k-\omega_q-\omega)t - i\,\mathrm{Sin}(\omega_k-\omega_q-\omega)t - 1\right|^2$$

$$|a_q(t)|^2 \approx \frac{2|H^+_{kq}|^2}{h^2(\Delta\omega-\omega)^2} \left[1 - \mathrm{Cos}(\Delta\omega-\omega)t\right] \tag{A.48}$$

where

$$\Delta\omega = \omega_k - \omega_q \tag{A.49}$$

Then using the trigonometric equality

$$1 - \mathrm{Cos}\theta = 2\,\mathrm{Sin}^2\frac{\theta}{2} \tag{A.50}$$

equation (A.48) reduces to

$$P_{k\to q}(t) \simeq \frac{|H^{+}_{kq}|^{2}}{h^{2}} \frac{\mathrm{Sin}^{2}[\frac{1}{2}(\omega_k-\omega_q-\omega)t]}{[\frac{1}{2}(\omega_k-\omega_q-\omega)]^{2}} \qquad (A.51)$$

$P_{k\to q}(t)$ is the probability of stimulated resonant emission. Similarly, when $E_k<E_q$ the second term in (A.46) dominates and the probability of (stimulated) resonant abosorption is

$$P_{k\to q}(t) \simeq \frac{|H^{-}_{kq}|^{2}}{h^{2}} \frac{\mathrm{Sin}^{2}[\frac{1}{2}(\omega_k-\omega_q+\omega)t]}{[\frac{1}{2}(\omega_k-\omega_q+\omega)]^{2}} \qquad (A.52)$$

From equations (A.40) and (A.44)

$$H^{+}_{kq} = <\psi_q(\bar{r})|\bar{U}_{op}\cdot\bar{E}^{+}|\psi_k(\bar{r})> \qquad (A.53)$$

Using (A.35) yields

$$\bar{U}_{op}\cdot\bar{E}^{+} = \bar{U}_{op}\cdot e^{i\bar{K}\cdot\bar{R}_o}[E^{o}_{x}\,\bar{a}_x + E^{o}_{y}\,\bar{a}_y + E^{o}_{z}\,\bar{a}_z] \qquad (A.54)$$

Defining

$$\bar{E}^{o} = E^{o}_{x}\,\bar{a}_x + E^{o}_{y}\,\bar{a}_y + E^{o}_{z}\,\bar{a}_z \qquad (A.55)$$

and substituting (A.54), (A.55) into (A.53) gives

$$H^{+}_{kq} = <\psi_q(\bar{r})|\bar{U}_{op}\cdot e^{i\bar{K}\cdot\bar{R}_o}\,\bar{E}^{o}|\psi_k(\bar{r})> \qquad (A.55)$$

$$|H^{+}_{kq}|^{2} = |e^{i\bar{K}\cdot\bar{R}_o}|^{2}|<\psi_q(\bar{r})|\bar{U}_{op}\cdot\bar{E}^{o}|\psi_k(\bar{r})>|^{2} \qquad (A.56)$$

$$|H^{+}_{kq}|^2 = |< \psi_q(\overline{r})|\overline{U}_{op} \cdot \overline{E}^o|\psi_k(\overline{r}) >|^2 \qquad (A.57)$$

Equation (A.57) may be substituted into (A.51) or (A.52) if the need arises.

The intensity of a charge-transfer spectrum is proportional to the square of the electronic transition moment as defined by equation (2.76). This is proved with the derivation of equations (A.51), (A.52), and (A.57). Using (A.21) and (A.55).

$$\overline{U}_{op} \cdot \overline{E}^o = E^o_x U_x + E^o_y U_y + E^o_z U_z \qquad (A.58)$$

Further, from (A.17) and (A.55) it is seen that, by definition, $\overline{E}_o$ is independent of the spatial coordinates. Therefore, using the definitions (A.30) to (A.32),

$$< \psi_q(\overline{r})|\overline{U}_{op} \cdot \overline{E}_o|\psi_k(\overline{r}) > = E^o_x < U_{kqx} > + E^o_y < U_{kqy} > + E^o_z < U_{kqz} > \qquad (A.59)$$

Considering the case where the electric field is homogeneous leads to the further simplification

$$E^o_x = E^o_y = E^o_z = E^o_f \qquad (A.60)$$

Then

$$< \psi_q(\overline{r})|\overline{U}_{op} \cdot \overline{E}_o|\psi_k(\overline{r}) > = E^o_f\{< U_{kqx} > + < U_{kqy} > + < U_{kqz} >\} \qquad (A.61)$$

Hence

$$|H^{+}_{kq}|^{2} = |E^{o}_{f}|^{2}|\{< U_{kqx} > + < U_{kqy} > + < U_{kqz} >\}|^{2} \qquad (A.62)$$

Equations (A.51), (A.52) and (A.62) show that the probability that a stimulated emission or absorption transition occurs (i.e. the intensity of the spectrum) depends, among other things, on the intensity of the electromagnetic field and the transition moment. In the derivation above the transition moment was assumed to be derived solely from the dipole moment of the molecule. This need not be the case, however, and by inclusion of quadrupole electric, magnetic dipole, etc., energy interaction terms in the perturbation Hamiltonian (see equation A.20), the intensities due to quadrupole, magnetic dipole, etc., transitions may be derived in an analogous manner. As pointed out previously, though, such transition probabilities are generally orders of magnitude smaller than electric dipole transition moments.

A.1.4. Einstein's Treatment of Spontaneous Emission [147,148,149]

The derivations above do not apply to spontaneous emission which is emission of electromagnetic radiation by an excited atom or molecule into empty space even in the absence of any other source of electromagnetic radiation. This is a shortcoming of the classical treatment of electromagnetic radiation. It can be shown that in a more complete treatment [142], with the field quantized, spontaneous emission would be accounted for in a natural way, together with the phenomena of stimulated emission and absorption.

A simpler approach due to Einstein [147] and based on thermodynamics may also be used to treat spontaneous emission. In this approach sponteneous emission is postulated, a rate ascribed to it and it is assumed that the matter is in thermal equilibrium with a blackbody thermal radiation field at temperature T [148,149].

It is assumed that the rates (sec^{-1}) at which the induced absorption and emission occur are proportional to the energy density per unit frequency, ρ, ($erg\ am^{-3}Hz^{-1} = erg\ cm^{-3}sec$) in the incident (perturbing) electromagnetic field. (This assumption can be verified by taking the perturbation treatment described above a step further [17]. This will be done below.) The constants of proportionality are the Einsten B coefficients. Hence

$$R_{k\to q} = B_{kq}\ \rho\ (sec^{-1}) \tag{A.63}$$

$$R_{q\to k} = B_{qk}\ \rho\ (sec^{-1}) \tag{A.64}$$

If $E_k > E_q$ then $R_{k\to q}$ is the rate of stimulated emission, B_{kq} is the *Einstein B Coefficient of Stimilated Emission*, $R_{q\to k}$ is the rate of (stimulated) absorption and B_{qk} is the *Einstein B Coefficient of Absorption*. (The units of B are therefore $erg^{-1}cm^{+3}sec^{-2}$.) A rate of spontaneous emission which is independent of any electromagnetic field is now postulated in the form of the *Einstein A Coefficient of Spontaneous Emission*. (The units of A are sec^{-1}). The A coefficient is the inverse of the spontaneous lifetime (in sec) associated with any transition $E_k \to E_q$ [148].

The situation where the atoms or molecules under consideration are in thermal equilibrium with a blackbody thermal radiation field at temperature T is now considered.

Let the densities of molecules in states k and q be $N_k(cm^{-3})$ and $N_q(cm^{-3})$ respectively. The assumption of equilibrium then requires

$$N_k[A_{kq} + \rho B_{kq}] = N_q B_{qk}\rho \quad (cm^{-3}sec^{-1}) \tag{A.65}$$

where as a further simplification a two level (k and q) molecular system is assumed.

ρ is assumed to be blackbody thermal radiation and is consequently governed by Planck's Law and given by [150]

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/KT}-1} \qquad (\text{erg cm}^{-3}\text{sec}) \qquad (A.66)$$

where ν is the frequency of radiation, h the Planck Constant, K the Boltzmann constant, T the absolute temperature and c the velocity of light.

Since the molecular system is assumed to be in thermal equilibrium the ratio N_k/N_q is given by the Boltzmann factor [150,151]

$$\frac{N_k}{N_q} = e^{-h\nu/KT} \qquad (A.67)$$

(We have assumed here that the molecular system is interacting with resonance radiation, i.e. the quantum energy separation between E_k and E_q is hν where ν is the radiation frequency under consideration in equation (A.66)).

Using (A.66) and (A.67) in (A.65) results in

$$\frac{8\pi h\nu^3}{c^3(e^{h\nu/KT}-1)} = \frac{A_{kq}}{B_{qk}e^{h\nu/KT}-B_{kq}} \qquad (A.68)$$

Equation (A.68) holds if

$$B_{kq} = B_{qk} \qquad (\text{erg}^{-1}\text{cm}^3\text{sec}^{-2}) \qquad (A.69)$$

and $$\frac{A_{kq}}{B_{kq}} = \frac{8\pi\nu^3 h}{c^3} \qquad (\text{erg cm}^{-3}\text{sec}) \qquad (A.70)$$

APPENDIX II

GROUP THEORETICAL IDENTIFICATION OF NON-ZERO ENERGY MATRIX ELEMENTS [61]

The Hamiltonian operator for any molecule must have the full symmetry of the system. It is simply an operator expression for the energy of the molecule and clearly, the energy of the molecule cannot change in either sign or magnitude as a result of a symmetry operation. The Hamiltonian, H, therefore belongs to the totally symmetric representation of the molecular point group.

Further there exists a theorem in group theory [61] which states that the representation of a direct product, Γ_{AB}, will contain the totally symmetric representation only if the irreducible representation Γ_A is identical to the irreducible representation Γ_B.

From these two statements it can be shown that an energy integral $< \psi_j | H | \psi_i >$ may be non zero only if ψ_i and ψ_j belong to the same irreducible representation of the molecular point group of the system described by these wavefunctions.

It can also be shown [61] than an electric dipole transition will be allowed with x,y, or z polarization if the direct product of the representations of the two states concerned is or contains the irreducible representation to which x,y or z, respectively, belongs.

$$f = 4.6 \times 10^{-9} \int \Sigma \, d\nu \qquad (A.3.5)$$

This is usually approximated as

$$f = 4.6 \times 10^{-9} \, \Sigma_{max} \, \Delta\nu_{1/2} \qquad (A.3.6)$$

where $\Delta\nu_{1/2}$ (cm^{-1}) is the bandwidth of the line and Σ_{max} the molar extinction coefficient (litre cm^{-1} $mole^{-1}$).

It can be shown that [129]

$$f \approx 1.5 \, (g_u/g_1)(1/\nu^2)(1/\tau^o) \qquad (A.3.7)$$

Here f is the oscillator strength in absorption, τ^o is the intrinsic lifetime of the reverse emission, g_1 is the multiplicity of the lower state and g_u multiplicity of the upper state. "Intrinsic emission lifetime" here implies the lifetime of an excited state which is depopulated by spontaneous emission only. [129]

From equations (A.4.7), (A.4.6) and (A.4.4)

$$\sigma = 1.24 \, \frac{g_u}{g_1} \, \frac{1}{\Delta\nu \cdot \nu^2} \, \frac{1}{\tau^o} \times 10^{-10} \quad (cm^2) \qquad (A.3.7)$$

when τ^o is in sec.

Consider pyrrole-oxygen CT emission (at approximately 4.5ev=36,000 cm^{-1} $=\nu$). Let $\Delta\nu$=4000 cm^{-1} and Σ=100 liters cm^{-1} $mole^{-1}$ (which are typical values, see [51] and [49]) then from (A.4.4) $\sigma \approx 3.8 \times 10^{-17}$ cm^2. From (A.3.7) this leads to a value of $\tau^o \approx 0.6 \times 10^{-6}$ sec. This is the approximate spontaneous emission lifetime of the pyrrole-oxygen contact CT fluorescence band.

APPENDIX III

OSCILLATOR STRENGTHS, CROSS-SECTIONS AND EXTINCTION COEFFICIENTS

A monochromatic beam of radiation of initial intensity I_i passing through a medium of thickness d cm emerges with an intensity I governed by [155,156]

$$I = I_i \; 10^{-\Sigma[M]d} \qquad (A.3.1)$$

where [M] is the molar concentration (moles/liter) of the absorbing species and Σ is defined as the *molar extinction coefficient* (liters cm^{-1} $mole^{-1}$). This follows from the well known relation [155]

$$I = I_i \; e^{-\mu d} \qquad (A.3.2)$$

where μ is the *absorption coefficient* (cm^{-1}).

Defining an absorption cross-section σ (cm^2) as

$$I = I_i \; e^{-\sigma n' d} = I_i \; e^{-\mu d} \qquad (A.3.3)$$

where n' is the density (cm^{-3}) of the absorbing species then it can be shown [155] that

$$\sigma = 3.81 \times 10^{19} \; \Sigma \; (cm^2) \qquad (A.3.4)$$

Here Σ is the molar extinction coefficient in liters cm^{-1} mol^{-1}.

The *Oscillator Strength*, f, which is a measure of the intensity of a radiative transition is given by [156-160]

The corresponding value of spontaneous emission lifetime for the benzene-oxygen contact CT fluorescence is approximately 0.5×10^{-6} sec (obtained by using $\nu = 45{,}000$ cm^{-1} = 5.6 ev, $\Delta\nu = 4{,}000$ cm^{-1}, $\Sigma = 100$ liters cm^{-1} mole^{-1} and $\sigma = 3.8 \times 10^{-17}$ cm^{2}).